

MOLECULAR MULTIPOLE MOMENTS AND THEIR PERFORMANCE
IN THE SELF-CONSISTENT REACTION FIELD MODEL

By

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To the Clbhs

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TABLE OF CONTENTS

ACKNOWLEDGMENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	ix
CHAPTERS	
1 INTRODUCTION	1
2 THE EVALUATION OF ELECTRIC MULTIPOLE MOMENT INTEGRALS OVER SLATER-TYPE ORBITALS	8
Introduction	8
Preliminary Considerations	9
Method	14
Discussion and Conclusions	33
3 THE CALCULATION OF MOLECULAR ELECTRIC MULTIPOLE MOMENTS	39
Definitions of Electric Multipole Moments	39
The Theory and Calculation of Molecular Orbitals	47
Some Calculated Molecular Multipole Moments	57
4 A SELF-CONSISTENT REACTION FIELD MODEL INCLUDING HIGH MOLECULAR ELECTRIC MULTIPOLE MOMENTS APPLIED TO THE CALCULATION OF MOLECULAR ELECTRONIC SPECTRA	71
The Reaction Field	71
The Interaction Energy in a Reaction Field	74
The Self-Consistent Reaction Model	75
The Configuration Interaction Calculation for Electronic Spectra	78
Results	87

5	CONCLUSIONS	100
	REFERENCES	105
	BIOGRAPHICAL SKETCH	111

LIST OF TABLES

Table 2-1: Percentage of Cartesians needed to Compute	38
Table 3-2: The Conversion Factors for 1 a.u. Multipole Moments	63
Table 3-3: Calculated Multipole Moments of H ₂ O	64
Table 3-4: Calculated Multipole Moments of Benzene	66
Table 3-5: Calculated Multipole Moments of Hexafluorobenzene	67
Table 3-6: Calculated Multipole Moments for Pyrazine in Water Solution	68
Table 4-7: H ₂ O solvent cost energy convergence in H ₂ O solution	92
Table 4-8: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory A.	93
Table 4-9: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory A1.	94
Table 4-10: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory B.	95
Table 4-11: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory B1.	96
Table 4-12: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory C.	97
Table 4-13: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory C1.	98
Table 4-14: Pyrazine $n - \pi^*$ Solvent Shift (cm-1): From Acetonitrile to Diethyl Ether. .	99

LIST OF FIGURES

Figure 1:	Rotation From Ellipsoidal Coordinate to Molecular Frame	36
Figure 2:	Flow chart of the HIMO computational program	37
Figure 3:	Input Molecular Orientations for Multipole Moment Calculations.	69
Figure 4:	Dimer Structures of Hexafluorobenzene-Benzene and Benzene-Benzene Based on Multipole Moment Interpretations	70
Figure 5:	Spherical Cavity Model	90
Figure 6:	Solvent Shift Dependence on Cavity Radii: C1 theory for acetone.	91

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Molecular electric multipole moments are calculated to high orders using the semiempirical Intermediate Differential Overlap (INDO) wavefunction at the Hartree-Fock level of theory. A general approach is developed for multipole moment integrals arising in computations using Slater-type orbitals (STO). A computational package implementing this approach is produced in this study and in our experience it is fast and reliable. Molecular multipole moments calculated with the existing INDO minimum basis set agree well with results in the available literature.

Calculated molecular multipole moments are included in the Self-Consistent Reaction Field (SCRF) model through the first order multipole expansion of electrostatic potentials between solute molecules and solvent dielectric media. Computations are implemented

in the Zerner's INDO (ZINDO) package to calculate solvent shifts of electronic spectra with the parametrized Configuration Interaction Singles (CIS) method. Spectroscopic shifts previously not accounted for by the Onsager term are produced in good agreement with experiment by using the newly developed theories C and C1. Multipole expansion convergence, cavity radius dependence, and other aspects of the SCRF model are studied and discussed.

CHAPTER 1 INTRODUCTION

Much chemistry is understood by simple interpretations based on dipole moments; even more is understood by using the quadrupole moments. In fact, a study of multipole moments is a popular, and arguably the most effective, language to address a variety of phenomena at the molecular level. However, in practice this has been a language with very limited vocabulary because a chemist can measure only dipole and quadrupole moments of molecules with any accuracy. Understanding of more subtle molecular interactions, structure, and physical and chemical behavior must resort to an examination of higher order multipole moments that, regrettably, have not been obtainable from experiment. In recent years, the need for high order molecular multipole moments has become pressing due to the rapid development in molecular dynamics simulations [1], computation of high order molecular polarizabilities [2–4], molecular optical and magnetic properties [5–8], intermolecular force theory in terms of the London series [4, 7, 9–13], and the quantum mechanical solvent effect in the formalism of the self-consistent reaction field theory [14–16].

The experimentalist has not been able to meet this need, and it is reasonable to believe this situation will remain unchanged for some time to come. To date quadrupole moments

are the highest-order multipole moments actually measured using a method that was established thirty-five years ago [17]. These measurements still contain great experimental errors, and in some cases even the sign is uncertain. Because multipole moments traditionally bear named units, there has been a great incentive for the measurement of high order moments! Yet even with this incentive there has been no breakthroughs.

On the theoretical “front” the challenge posed by calculating high-order multipole moments is taken with enthusiasm and varied sophistication. After half a century of development modern quantum mechanical calculation has finally come of age in attacking a variety of problems that are unsolvable experimentally. With computational resources readily available ranging from personal computer to massively parallel machines one can nowadays use well established and tested procedures to solve the Schrödinger equation for a given molecule or molecular system which gives an understanding of the underlying electronic structure in terms of molecular orbitals, which in turn, can be used to calculate desired electronic properties. By nature, molecular multipole moments are one-electron properties of a molecule. In theory, they can be calculated to any order we want, but current calculations have not exceeded the tenth order due to basis set reliability. Modern electronic structure theory is formulated to solve the Schrödinger equation in a basis set of finite dimension, which usually is expressed as linear combination of atomic-like orbitals. There are two kinds of prevailing atomic orbitals in the current

stage of quantum mechanical calculations: Slater-type orbital (STO) with form $e^{-\alpha r}$ and Gaussian-type Orbital (GTO) with the form $e^{-\alpha r^2}$. A molecular orbital description based on an STO or GTO basis can often give molecular dipole moments with greater precision than quadrupole moments because dipole moments are by and large caused by electronic density near the molecular region. For moments higher than quadrupole, it is known that basis set choice is very important [18], because high moments are very sensitive to electronic distributions in the outer molecular region, regions which are not important in the said variation of the energy calculated from the Schrödinger equation. Basis set effects are found to be far more important than correlation effect on these high moments [19, 20]. However, most multipole-moment calculations are carried out using Gaussian basis set; in fact we are not aware of any recent STO basis set calculations on moments higher than quadrupole for polyatomic molecules. It is well understood that the proper choice for molecular electric property calculations is STO, because STO has the correct long range behavior. But the use of STO in solving the Schrödinger equation is very difficult, and even today represents an unsolved problem for certain type of integrals. In practice in approximate and semiempirical models not all STO integrals are evaluated; rather some of them are parameterized by experimental data when they can be tangibly related to observed physical properties. Today, however, all *ab initio* models use GTOs in place of STOs to evaluate all the integrals necessary. The use of GTOs in

molecular orbital theory is a practical choice to facilitate integration, but not a desirable one. Multipole moment integrals are conveniently worked out in GTOs by Matsuoka [21], Augspurger and Dykstra [22], and Mikkelsen *et al.* [15]. A study of these moments using numerical techniques can be found in the calculations of Pyykko [20]. High moment integrals over STO are not well studied, although they would not appear to be particularly intractable. Originally molecular orbital theory of polyatomic molecules was formulated using STO basis sets and a series of now classical work on STO integrals was carried out by Mulliken, Rieke, Orloff and Orloff [23], Roothaan [24, 25], Ruedenberg [26], and Ruedenberg, Roothaan and Jaunzemis [27]. Local dipole moment integrals were formulated by Hamilton using C functions [28]. Quadrupole moment integrals were included in the study by Wahl, Cade, and Roothaan [29], and implemented by Bagus, Liu, McLean and Yoshimine [30] for linear molecules. A specific and detailed treatment of dipole moment integrals for polyatomic molecules was presented by Rein, Clarke and Harris [31], which was extended to handle quadrupole moment integrals by Rabinowitz and Rein [32], and octopole moment integrals by Swisler and Rein [33]. We have not found studies of higher moment integrals over STO basis set for polyatomic molecules; Rather, such studies are carried out with GTO basis set. The popular use of Gaussian basis set here has an inherent drawback: multipole moment description of molecular phenomena is a good approximation to the underlying electrostatic interaction only at

long range, but at long range Gaussian orbitals are known to fall too sharply. For this reason there have been *ab initio* calculations using Gaussian basis set that are then fitted to STOs to study long-range interactions [34].

An important interaction is the electrostatic interaction between a solute molecule and its solvent. It is important as chemistry seldom takes place in a vacuum while quantum chemistry usually considers only the vacuum environment. The theoretical treatment of the thermodynamic and kinetic solvent effects can be undertaken by means of force-field methods [35], wherein a classical Hamiltonian is used to treat both solute and solvent molecules in the framework of molecular dynamics (MD) and Monte Carlo (MC) simulations. However, these methods do not take account of the mutual solute-solvent polarization, which is accounted for by quantum mechanical (QM) methods to allow charge redistributions. There are three major approaches in the QM calculations of the solvent effect: the supermolecular method [36, 37] the mixed QM- molecular mechanics method (QM-MM) [38, 39], and the self-consistent reaction field (SCRF) method [40–47]. All three treat the solute molecule quantum mechanically, and the differences lie in the description of the solvent. In the supermolecule model, the solvent molecules are also described at the QM level, but only a few of them can be included explicitly. In the QM-MM approach the solvent molecules are treated as classical entities with point dipoles or partial atomic charges, and the dynamics of the solute-solvent system is accounted for by

MD or MC calculations. Finally, the SCRF model considers the solvent to be a continuum dielectric medium, which reacts against the solute charge distribution generating a reaction field, which is then included as a perturbation term in the vacuum Hamiltonian of a solute molecule. The SCRF model, although it lacks microscopic representation of the solvent molecules, is an inexpensive method to obtain solute molecular orbitals in solution, and therefore is an excellent approach to examine spectroscopic shift and molecular property changes of a chromophore in solution, and indeed, from the experience in this laboratory, these examinations reveal a great deal about molecular electronic structure in solution. However, the implementation of the SCRF model in our studies has not been complete enough to study a broader range of molecules, particularly those that do not possess permanent dipole and quadrupole moments. The impediment, of course, lies in the lack of reliable computation of accurate high order multipole moments that describe the solute-solvent interaction in the perturbation of the vacuum Hamiltonian and the conceptual difficulty in the high order formalism.

Solvation has received a great deal of interest in the quantum chemistry community, and some vigorous research to tackle the associated problems has been done in this group over the years [48, 16, 49]. Hard pressed by the growing needs in the course of this effort, the work presented in this thesis is carried out and it proves to be quite successful in addressing the problem. Chapter 2 establishes the method of computing multipole

moment integrals necessary in this study [50]. Chapter 3 surveys the conventions and presents calculational results of molecular multipole moments. Chapter 4 recaps the essence of SCRF and electronic spectra theory, and gives the UV-Vis spectral shift in solution as calculated by our method. And, finally, Chapter 5 gives the conclusion and future outlook of this work.

CHAPTER 2

THE EVALUATION OF ELECTRIC MULTIPOLE MOMENT INTEGRALS OVER SLATER-TYPE ORBITALS

Introduction

As will be surveyed in Chapter 3, there exist definitions of electric multipole moment in the literature. Nevertheless, and as confusing as it may seem, these different forms are related to each other! Let us then choose one of them

$$M_{l,m} = r^l \left[\frac{4\pi}{2(l+1)} \right]^{1/2} Y_{l,m}(\theta, \phi) \quad (2.1)$$

where $Y_{l,m}(\theta, \phi)$ is a spherical harmonics. Following Rabinowitz and Rein [32], it is now convenient to define a primitive multipole moment operator as

$$M_{i,j,k} = x^i y^j z^k \quad (2.2)$$

with its expectation values giving all the integrals necessary to compute the multipole moments defined in equation (2.1). The computation of the nuclear contribution to the multipole moments is straightforward, simply replacing the electronic coordinates x, y, z in $M_{i,j,k}$ with the nuclear ones X, Y, Z . We therefore consider only the electronic contribution in this chapter.

The integration of a primitive multipole moment operator of equation (2.2) over a pair of chosen basis functions is in essence a one-electron, and at most, three-center

computation. A method of evaluating integrals of this nature is generally outlined by Harris and Michels [51], Steinborn and Ruedenberg [52], and Guseinov and Sadichov [53]. These traditional approaches all invoke translational, rotational and combinational properties of spherical harmonics of various kinds that are nicely examined in the works of Steinborn and Ruedenberg [54], and Steinborn [55]. This chapter presents a novel method of evaluating multipole-moment integrals over STO basis functions. We will show explicit formulas for up to hexadecapole moment in a basis set that includes up to g orbitals. The method, although somewhat tedious, is completely generalizable and results in very fast computer code.

Preliminary Considerations

Cartesians and Tesseral Harmonics

An STO is usually given by

$$\chi_{n,l,m} = \left[\frac{(2\zeta)^{2n+1}}{(2n)!} \right]^{1/2} r^{n-1} e^{-\zeta r} \bar{Y}_l^m(\theta, \phi) \quad (2.3)$$

where $\bar{Y}_l^m(\theta, \phi)$ are the normalized real spherical harmonics [56], and the square root factor is the normalization constant for the radial component. We regroup these terms as

$$\chi_{n,l,m} = \left[\frac{(2\zeta)^{2n+1}}{(2n)!} \right]^{1/2} r^{n-l-1} e^{-\zeta r} [r^l \bar{Y}_l^m(\theta, \phi)] \quad (2.4)$$

which allows a convenient representation of the angular part in terms of Cartesian components. The quantities in the second bracket are known as Tesseral harmonics [57],

which we note as

$$l_{\overline{m}} = \left[r^l \overline{Y}_l^m(\theta, \phi) \right] \quad (2.5)$$

where l has its usual meaning ($l = 0, 1, 2, 3 \dots$ for s, p, d, f, ...) and \overline{m} enumerates the real components obtained from adding $Y_l^m \pm Y_l^{-m}$.

We define a product of the powers of x, y and z to be a Cartesian,

$$(i, j, k) = x^i y^j z^k \quad (2.6)$$

where i, j, and k are integers. In this notation the normalized Tesseral harmonics are written below up to g type [58],

s harmonic:

$$s = \sqrt{\frac{1}{4\pi}}(0, 0, 0).$$

p harmonics:

$$p_x = \sqrt{\frac{3}{4\pi}}(1, 0, 0), \quad p_y = \sqrt{\frac{3}{4\pi}}(0, 1, 0), \quad p_z = \sqrt{\frac{3}{4\pi}}(0, 0, 1).$$

d harmonics:

$$d_{z^2} = \sqrt{\frac{5}{16\pi}}[2(0, 0, 2) - (2, 0, 0) - (0, 2, 0)],$$

$$d_{x^2-y^2} = \sqrt{\frac{15}{16\pi}}[(2, 0, 0) - (0, 2, 0)],$$

$$d_{xy} = \sqrt{\frac{15}{4\pi}}(1, 1, 0), \quad d_{xz} = \sqrt{\frac{15}{4\pi}}(1, 0, 1), \quad d_{yz} = \sqrt{\frac{15}{4\pi}}(0, 1, 1).$$

f harmonics:

$$f_{z^3} = \sqrt{\frac{63}{16\pi}}[\frac{2}{3}(0, 0, 3) - (2, 0, 1) - (0, 2, 1)],$$

$$f_{xz^2} = \sqrt{\frac{21}{32\pi}}[4(1, 0, 2) - (3, 0, 0) - (1, 2, 0)],$$

$$f_{yz^2} = \sqrt{\frac{21}{32\pi}}[4(0, 1, 2) - (2, 1, 0) - (0, 3, 0)],$$

$$f_{z(x^2-y^2)} = \sqrt{\frac{105}{16\pi}}[(2, 0, 1) - (0, 2, 1)], \quad f_{xyz} = \sqrt{\frac{105}{4\pi}}(1, 1, 1),$$

$$f_{x^3-3xy^3} = \sqrt{\frac{35}{32\pi}}[(3, 0, 0) - 3(1, 2, 0)],$$

$$f_{3x^2y-y^3} = \sqrt{\frac{35}{32\pi}}[3(2, 1, 0) - (0, 3, 0)].$$

g harmonics:

$$g_{z^4} = \frac{9}{16\sqrt{\pi}}[(4, 0, 0) + 2(2, 2, 0) + (0, 4, 0) - 8(2, 0, 2) - 8(0, 2, 2) + \frac{8}{3}(0, 0, 4)],$$

$$g_{xz^3} = \frac{9}{8}\sqrt{\frac{10}{\pi}}[\frac{4}{3}(1, 0, 3) - (3, 0, 1) - (1, 2, 1)],$$

$$g_{yz^3} = \frac{9}{8}\sqrt{\frac{10}{\pi}}[\frac{4}{3}(0, 1, 3) - (2, 1, 1) - (0, 3, 1)],$$

$$g_{z^2(x^2-y^2)} = \frac{3}{8}\sqrt{\frac{5}{\pi}}[-(4, 0, 0) + (0, 4, 0) + 6(2, 0, 2) - 6(0, 2, 2)],$$

$$g_{xyz^2} = \frac{3}{4}\sqrt{\frac{5}{\pi}}[6(1, 1, 2) - (3, 1, 0) - (1, 3, 0)],$$

$$g_{z(x^3-3xy^3)} = \frac{3}{8}\sqrt{\frac{70}{\pi}}[(3, 0, 1) - 3(1, 2, 1)],$$

$$g_{z(3x^2y-y^3)} = \frac{3}{8}\sqrt{\frac{70}{\pi}}[3(2, 1, 1) - (0, 3, 1)],$$

$$g_{x^2y^2} = \frac{3}{16}\sqrt{\frac{35}{\pi}}[(4, 0, 0) - 6(2, 2, 0) + (0, 4, 0)],$$

$$g_{xy(x^2-y^2)} = \frac{3}{4}\sqrt{\frac{35}{\pi}}[(3, 1, 0) - (1, 3, 0)].$$

Coordinate Systems and The Rotational Matrix

The evaluation of STO integrals is usually first carried out locally regardless of the orientation of molecular input that defines a molecular frame coordinate, and then through rotational transform the integral value is obtained in the coordinate of the molecular frame. The two atomic basis functions are usually defined in the individual atomic coordinate systems. The relation between two individual atomic coordinate systems is established through a third coordinate system centered in between the two atoms. The explicit formulas to be established form the basis of the transformation from a local integral value to that in the molecular frame.

The STO basis functions are generally associated with centers (usually on nuclei) denoted as A, B, The center of a primitive moment operator of equation (2.6) is denoted as O. Lower-case subscripts a, b, and o specify the vector components measured from the centers A, B and O, respectively. Unlike Cartesian Gaussians, STO two center integrals are generally evaluated over a local system (see Figure 1) with the axis between the two centers defining the local Z, Z_a , and Z_b axes, with the local X, X_a , X_b , and Y, Y_a , Y_b axes parallel. Here the upper-case notations X, Y, Z represent axes in the local system. The Z_a and Z_b axes are either pointing at each other, or are directed in the same direction. We adapt the latter, as shown in Figure 1.

With the origin of the Cartesian coordinate system [X, Y, Z] placed halfway between

the two basis function centers A and B, the local system described above is used to define a prolated spheroidal, or, ellipsoidal coordinate system focused on A and B, respectively [52]. Adapting the definition and notations of reference [52], we list some important relations below for an ellipsoidal coordinate system,

$$\begin{aligned}
 r_a &= \frac{R}{2}(\xi + \eta), \quad r_b = \frac{R}{2}(\xi - \eta), \\
 x_a &= x_b = \frac{R}{2}\sqrt{(\xi^2 - 1)(1 - \eta^2)}\cos\phi, \\
 y_a &= y_b = \frac{R}{2}\sqrt{(\xi^2 - 1)(1 - \eta^2)}\sin\phi, \\
 z_a &= \frac{R}{2}(1 + \xi\eta), \quad z_b = \frac{R}{2}(1 - \xi\eta), \\
 d\tau &= \frac{R^3}{8}(\xi^2 - \eta^2)d\xi d\eta d\phi.
 \end{aligned} \tag{6}$$

The integrals evaluated in a local ellipsoidal coordinate system then need to be back transformed into a laboratory, or molecular based coordinate system, which we define to be the molecular frame $[x', y', z']$. The rotation necessary for this transformation is based on the directional cosine and sine, (see Figure 1)

$$\begin{aligned}
 \cos\theta &= \frac{\Delta z'}{R}, \\
 \sin\phi &= \frac{\Delta y'}{\sqrt{\Delta x'^2 + \Delta y'^2}}.
 \end{aligned} \tag{7}$$

and the rotation matrix $R(\theta, \phi)$ can be obtained in two steps:

i) rotate about the y axis to align the z axis: $R_1(\theta)$,

$$\begin{pmatrix} X'' \\ Y'' \\ Z'' \end{pmatrix} = R_1(\theta) \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} \quad (8)$$

ii) rotate about the z'' axis to align the x'' and y'' axes: $R_2(\phi)$,

$$\begin{pmatrix} X' \\ Y' \\ Z' \end{pmatrix} = R_2(\phi) \begin{pmatrix} X'' \\ Y'' \\ Z'' \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} X'' \\ Y'' \\ Z'' \end{pmatrix} \quad (9)$$

the final rotation matrix based on matrix equations ((8)) and ((9)) is therefore

$$R(\theta, \phi) = R_2(\phi)R_1(\theta) = \begin{pmatrix} \cos\theta\cos\phi & -\sin\phi & \sin\theta\cos\phi \\ \cos\theta\sin\phi & \cos\phi & \sin\theta\sin\phi \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \quad (10)$$

Method

Translation of Centers

The most common way to proceed from here is, assuming the moment definition of equation (2.1), to evaluate the integrals such as

$$I = \int d\Omega Y_l^{m'}(\theta_a, \phi_a) Y_{l''}^{m''}(\theta_o, \phi_o) Y_{l'''}^{m'''}(\theta_b, \phi_b) \quad (2.12)$$

and to translate the center O to the center A or B with the lowest l value, say, center B with l''' . Making use of the translational property of spherical harmonics [44] and Gaunt coefficients [45] this yields an integral with sigma ($m = 0$), pi ($m = 1$), delta ($m = 2$), phi ($m = 3$), etc., components. The maximum m component required is then the lesser of $l'' + l'''$ or l' , i.e.,

$$I = \sum_{m=0}^{\min(l''+l''', l')} R_m I_m = R_\sigma I_\sigma + (R_\pi + R_{\pi'}) I_\pi + (R_\delta + R_\delta) I_\delta + \dots \quad (2.13)$$

where the R_m 's are the factors due to rotating the integral back to the molecular frame, and the I_m 's are the appropriate integrals evaluated in the local frame. Note that $R_m = R_{m(A)m(B)}$ — each center must be rotated, and there are two pi components, two delta components, etc.

In this study we will translate the angular components of both the operator and the orbital centered on A to B. By doing so, center A will only have a sigma component and equation (2.13) will have the simple appearance of

$$I = R_{\sigma(B)} \tilde{I}_{\sigma} \quad (2.14)$$

We will show that the evaluation of \tilde{I}_{σ} and the rotation $R_{\sigma(A)}R_{\sigma(B)} = R_{\sigma(B)}$ are very simple. The use of equation (2.14) rather than equation (2.13), and its simplicity, are at the heart of this work.

Considering a general laboratory coordinate system $[x, y, z]$ and a particular one $[x_a, y_a, z_a]$ centered at $A(a_x, a_y, a_z)$, we have

$$x_a = x - a_x$$

$$y_a = y - a_y \quad (12)$$

$$z_a = z - a_z$$

to translate the system $[x_a, y_a, z_a]$ to another one $[x_b, y_b, z_b]$ centered at $B(b_x, b_y, b_z)$

we write

$$x_a = x_b + (b_x - a_x) = x_b + \overline{ba}_x$$

$$x_a = y_b + (b_y - a_y) = y_b + \overline{ba}_y \quad (2.16)$$

$$y_a = z_b + (b_z - a_z) = z_b + \overline{ba}_z$$

An arbitrary Cartesian defined in the previous section is therefore translated from center A to center B by way of

$$\begin{aligned} x_a^i y_a^j z_a^k &= \sum_{r=0}^i \binom{i}{r} \overline{ba}_x^{i-r} x_b^r \sum_{s=0}^j \binom{j}{s} \overline{ba}_y^{j-s} y_b^s \sum_{t=0}^k \binom{k}{t} \overline{ba}_z^{k-t} z_b^t \\ &= \sum_{(r,s,t)=(0,0,0)}^{(i,j,k)} C_{r,s,t}(\overline{ba}_x, \overline{ba}_y, \overline{ba}_z) x_b^r y_b^s z_b^t \end{aligned} \quad (2.17)$$

The translations in terms of equation (2.17) enable a multipole moment integral, apart from a normalization factor, to assume the following form,

$$\begin{aligned} \langle M_{l,m,n} \rangle &= \langle r_a^{n_a-l_a-1} x_a^i y_a^j z_a^k e^{-\zeta_a r_a} | x_o^l y_o^m z_o^n | r_b^{n_b-l_b-1} x_b^e y_b^f z_b^g e^{-\zeta_b r_b} \rangle \\ &= \sum_{(r,s,t)=(0,0,0)}^{(i,j,k)} C_{r,s,t}(\overline{ba}_x, \overline{ba}_y, \overline{ba}_z) \sum_{(u,v,w)=(0,0,0)}^{(l,m,n)} C_{u,v,w}(\overline{bo}_x, \overline{bo}_y, \overline{bo}_z) \cdot \quad (2.18) \\ &\quad \cdot \langle r_a^{n_a-l_a-1} e^{-\zeta_a r_a} | r_b^{n_b-l_b-1} x_b^{e+r+u} y_b^{f+s+v} e^{-\zeta_b r_b} \rangle \end{aligned}$$

where center O(O_x, O_y, O_z) places the origin with which the multipole moment integral is evaluated.

In this development it is clear that a moment integral is a combination of overlap integrals, which, in terms of equation (2.18), are always between an s orbital and a higher

order orbital. The translation to achieve this is straightforward. However, the sixfold sum that appears in equation (2.18), if directly implemented, is computationally inefficient, as was first experienced by Taketa, Huzinaga and O-Ohata in their work on Gaussian integrals [46]. For this reason we translate an STO centered at $A(x_a, y_a, z_a)$ and the moment operator centered on $O(x_o, y_o, z_o)$ separately onto the center $B(x_b, y_b, z_b)$ using two sets of predetermined formulas. With the convention that all left-hand quantities in a formula are centered on A, and those on the right-hand side centered on B we list these formulas as follows:

Master formulas for STO translation:

$$l_m^A = \sum_{\mu} g_{\mu}^a(\overline{ba_x}, \overline{ba_y}, \overline{ba_z})(i, j, k)_{\mu}^B \quad (2.19)$$

$$p_x = \sqrt{\frac{3}{4\pi}}[\overline{ba_x}(0, 0, 0) + (1, 0, 0)] \quad (2.20)$$

$$p_y = \sqrt{\frac{3}{4\pi}}[\overline{ba_y}(0, 0, 0) + (0, 1, 0)] \quad (2.21)$$

$$p_z = \sqrt{\frac{3}{4\pi}}[\overline{ba_z}(0, 0, 0) + (0, 0, 1)] \quad (2.22)$$

$$d_{z^2} = \sqrt{\frac{5}{16\pi}}[(2\overline{ba_z}^2 - \overline{ba_x}^2 - \overline{ba_y}^2)(0, 0, 0) - 2\overline{ba_x}(1, 0, 0) - 2\overline{ba_y}(0, 1, 0) + \quad (2.23)$$

$$4\overline{ba_z}(0, 0, 1) - (2, 0, 0) - (0, 2, 0) + 2(0, 0, 2)]$$

$$d_{x^2-y^2} = \sqrt{\frac{15}{16\pi}}[(\overline{ba_x}^2 - \overline{ba_y}^2)(0, 0, 0) - 2\overline{ba_y}(0, 1, 0) + 2\overline{ba_x}(1, 0, 0) + \quad (2.24)$$

$$(2, 0, 0) - (0, 2, 0)]$$

$$d_{xy} = \sqrt{\frac{15}{4\pi}} [\bar{b}a_x \bar{b}a_y(0,0,0) + \bar{b}a_y(1,0,0) + \bar{b}a_x(0,1,0) + (1,1,0)] \quad (2.25)$$

$$d_{xz} = \sqrt{\frac{15}{4\pi}} [\bar{b}a_x \bar{b}a_z(0,0,0) + \bar{b}a_z(1,0,0) + \bar{b}a_x(0,0,1) + (1,0,1)] \quad (2.26)$$

$$d_{yz} = \sqrt{\frac{15}{4\pi}} [\bar{b}a_y \bar{b}a_z(0,0,0) + \bar{b}a_z(0,1,0) + \bar{b}a_y(0,0,1) + (0,1,1)] \quad (2.27)$$

$$f_{z^3} = \sqrt{\frac{7}{16\pi}} [(2\bar{b}a_z^3 - 3\bar{b}a_x^2 \bar{b}a_z - 3\bar{b}a_x^2 \bar{b}a_z)(0,0,0) - 6\bar{b}a_x \bar{b}a_z(1,0,0) - 6\bar{b}a_y \bar{b}a_z(0,1,0) + (6\bar{b}a_z^2 - 3\bar{b}a_x^2 - 3\bar{b}a_y^2)(0,0,1) - 3\bar{b}a_z(2,0,0) - 6\bar{b}a_x(1,0,1) - 3\bar{b}a_z(0,2,0) - 6\bar{b}a_y(0,1,1) + 6\bar{b}a_z(0,0,2) - 3(2,0,1) - 3(0,2,1) + 2(0,0,3)] \quad (2.28)$$

$$f_{xz^2} = \sqrt{\frac{21}{32\pi}} [(4\bar{b}a_x \bar{b}a_z^2 - \bar{b}a_x^3 - \bar{b}a_x \bar{b}a_y^2)(0,0,0) + (4\bar{b}a_z^2 - 3\bar{b}a_x^2 - \bar{b}a_y^2)(1,0,0) - 2\bar{b}a_x \bar{b}a_y(0,1,0) + 8\bar{b}a_x \bar{b}a_z(0,0,1) - 3\bar{b}a_x(2,0,0) - 2\bar{b}a_y(1,1,0) - \bar{b}a_x(0,2,0) + 8\bar{b}a_z(1,0,1) + 4\bar{b}a_x(0,0,2) - (3,0,0) - (1,2,0) + 4(1,0,2)] \quad (2.29)$$

$$f_{yz^2} = \sqrt{\frac{21}{32\pi}} [(4\bar{b}a_y \bar{b}a_z^2 - \bar{b}a_x^2 \bar{b}a_y - \bar{b}a_y^3)(0,0,0) - 2\bar{b}a_x \bar{b}a_y(1,0,0) + 8\bar{b}a_y \bar{b}a_z(0,0,1) + (4\bar{b}a_z^2 - \bar{b}a_x^2 - 3\bar{b}a_y^2)(0,1,0) - \bar{b}a_y(2,0,0) - 2\bar{b}a_x(1,1,0) - 3\bar{b}a_y(0,2,0) + 8\bar{b}a_z(0,1,1) + 4\bar{b}a_y(0,0,2) - (2,1,0) - (0,3,0) + 4(0,1,2)] \quad (2.30)$$

$$\begin{aligned}
f_{z(x^2-y^2)} = & \sqrt{\frac{105}{16\pi}} [\overline{ba}_z (\overline{ba}_x^2 - \overline{ba}_y^2) (0, 0, 0) + 2\overline{ba}_x \overline{ba}_z (1, 0, 0) - \\
& 2\overline{ba}_y \overline{ba}_z (0, 1, 0) + (\overline{ba}_x^2 - \overline{ba}_y^2) (0, 0, 1) + \overline{ba}_z (2, 0, 0) + \\
& 2\overline{ba}_x (1, 0, 1) - \overline{ba}_z (0, 2, 0) - 2\overline{ba}_y (0, 1, 1) + (2, 0, 1) - (0, 2, 1)]
\end{aligned} \tag{2.31}$$

$$\begin{aligned}
f_{xyz} = & \sqrt{\frac{105}{4\pi}} [\overline{ba}_x \overline{ba}_y \overline{ba}_z (0, 0, 0) + \overline{ba}_y \overline{ba}_z (1, 0, 0) + \overline{ba}_x \overline{ba}_z (0, 1, 0) + \\
& \overline{ba}_x \overline{ba}_y (0, 0, 1) + \overline{ba}_z (1, 1, 0) + \overline{ba}_y (1, 0, 1) + \overline{ba}_x (0, 1, 1) + (1, 1, 1)]
\end{aligned} \tag{2.32}$$

$$\begin{aligned}
f_{x^3-3xy^2} = & \sqrt{\frac{35}{32\pi}} [(\overline{ba}_x^3 - \overline{ba}_x \overline{ba}_y^2) (0, 0, 0) + 3(\overline{ba}_x^2 - \overline{ba}_y^2) (1, 0, 0) - \\
& 6\overline{ba}_x \overline{ba}_y (0, 1, 0) + 3\overline{ba}_x (2, 0, 0) - 6\overline{ba}_y (1, 1, 0) - \\
& 3\overline{ba}_x (0, 2, 0) + (3, 0, 0) - 3(1, 2, 0)]
\end{aligned} \tag{2.33}$$

$$\begin{aligned}
f_{3x^2y-y^3} = & \sqrt{\frac{35}{32\pi}} [(3\overline{ba}_x^2 \overline{ba}_y - \overline{ba}_y^3) (0, 0, 0) + 6\overline{ba}_x \overline{ba}_y (1, 0, 0) + \\
& 3(\overline{ba}_x^2 - \overline{ba}_y^2) (0, 1, 0) + 3\overline{ba}_y (2, 0, 0) + 6\overline{ba}_x (1, 1, 0) - \\
& 3\overline{ba}_y (0, 2, 0) + 3(2, 1, 0) - (0, 3, 0)]
\end{aligned} \tag{2.34}$$

$$\begin{aligned}
g_{z^4} = & \frac{3}{16\sqrt{\pi}} \{ (3\overline{ba}_x^4 + 6\overline{ba}_x^2\overline{ba}_y^2 + 3\overline{ba}_y^4 - 24\overline{ba}_y^2\overline{ba}_z^2 + 8\overline{ba}_z^4 - 24\overline{ba}_x^2\overline{ba}_z^2)(0, 0, 0) \\
& + (12\overline{ba}_x^3 + 2\overline{ba}_x\overline{ba}_y^2 - 48\overline{ba}_x\overline{ba}_z^2)(1, 0, 0) + 12(\overline{ba}_x^2\overline{ba}_y + \overline{ba}_y^3 - 4\overline{ba}_y\overline{ba}_z^2)(0, 1, 0) \\
& + 16(2\overline{ba}_z^3 - 3\overline{ba}_x^2\overline{ba}_z - 3\overline{ba}_y^2\overline{ba}_z)(0, 0, 1) + 6(3\overline{ba}_x^2 + \overline{ba}_y^2 - 4\overline{ba}_z^2)(2, 0, 0) \\
& + 24\overline{ba}_x\overline{ba}_y(1, 1, 0) - 96\overline{ba}_x\overline{ba}_z(1, 0, 1) + 6(\overline{ba}_x^2 + 3\overline{ba}_y^2 - 4\overline{ba}_z^2)(0, 2, 0) \\
& - 96\overline{ba}_y\overline{ba}_z(0, 1, 1) - 24(\overline{ba}_x^2 + \overline{ba}_y^2 - 2\overline{ba}_z^2)(0, 0, 2) + 12\overline{ba}_x[(3, 0, 0) + (1, 2, 0) \\
& - 4(1, 0, 2)] + 12\overline{ba}_y[(2, 1, 0) + (0, 3, 0) - 4(0, 1, 2)] - 16\overline{ba}_z[3(2, 0, 1) \\
& + 3(0, 2, 1) - 2(0, 0, 3)] + 3(4, 0, 0) + 6(2, 2, 0) - 24(2, 0, 2) + 3(0, 4, 0) \\
& - 24(0, 2, 2) + 8(0, 0, 4) \}
\end{aligned} \tag{2.35}$$

$$\begin{aligned}
g_{xz^3} = & \frac{3}{8} \sqrt{\frac{10}{\pi}} \left\{ \left(4\overline{ba_x} \overline{ba_z}^3 - 3\overline{ba_x}^3 \overline{ba_z} - 3\overline{ba_x} \overline{ba_y}^2 \overline{ba_z} \right) (0, 0, 0) + \left(4\overline{ba_z}^3 - 9\overline{ba_x}^2 \overline{ba_z} - 3\overline{ba_y}^2 \overline{ba_z} \right) \right. \\
& \cdot (1, 0, 0) - 6\overline{ba_x} \overline{ba_y} \overline{ba_z} (0, 1, 0) + 3 \left(4\overline{ba_x} \overline{ba_z}^2 - \overline{ba_x}^3 - \overline{ba_x} \overline{ba_y}^2 \right) (0, 0, 1) \\
& + 3(4\overline{ba_z}^2 - 3\overline{ba_x}^2 - \overline{ba_y}^2) (1, 0, 1) - 3\overline{ba_x} \overline{ba_z} [3(2, 0, 0) + (0, 2, 0) - 4(0, 0, 2)] \\
& - 6\overline{ba_y} \overline{ba_z} (1, 1, 0) - 6\overline{ba_x} \overline{ba_y} (0, 1, 1) + 3\overline{ba_z} [4(1, 0, 2) - (3, 0, 0) - (1, 2, 0)] \\
& + \overline{ba_x} [4(0, 0, 3) - 3(0, 2, 1) - 9(2, 0, 1)] - 6\overline{ba_y} (1, 1, 1) - 3(3, 0, 1) \\
& \left. - 3(1, 2, 1) + 4(1, 0, 3) \right\}
\end{aligned} \tag{2.36}$$

$$\begin{aligned}
g_{yz^3} = & \frac{3}{8} \sqrt{\frac{10}{\pi}} \left\{ \left(4\overline{ba_y} \overline{ba_z}^3 - 3\overline{ba_y}^3 \overline{ba_z} - 3\overline{ba_x}^2 \overline{ba_y} \overline{ba_z} \right) (0, 0, 0) + \left(4\overline{ba_z}^3 - 9\overline{ba_y}^2 \overline{ba_z} - 3\overline{ba_x}^2 \overline{ba_z} \right) \right. \\
& \cdot (0, 1, 0) - 6\overline{ba_x} \overline{ba_y} \overline{ba_z} (1, 0, 0) + 3 \left(4\overline{ba_y} \overline{ba_z}^2 - \overline{ba_y}^3 - \overline{ba_x}^2 \overline{ba_y} \right) (0, 0, 1) \\
& + 3(4\overline{ba_z}^2 - 3\overline{ba_y}^2 - \overline{ba_x}^2) (0, 1, 1) - 3\overline{ba_y} \overline{ba_z} [(2, 0, 0) + 3(0, 2, 0) - 4(0, 0, 2)] \\
& - 6\overline{ba_x} \overline{ba_z} (1, 1, 0) - 6\overline{ba_x} \overline{ba_y} (1, 0, 1) + 3\overline{ba_z} [4(0, 1, 2) - (0, 3, 0) - (2, 1, 0)] \\
& + \overline{ba_y} [4(0, 0, 3) - 3(2, 0, 1) - 9(0, 2, 1)] - 6\overline{ba_x} (1, 1, 1) - 3(0, 3, 1) \\
& \left. - 3(2, 1, 1) + 4(0, 1, 3) \right\}
\end{aligned} \tag{2.37}$$

$$\begin{aligned}
g_{z^2(x^2-y^2)} = & \frac{3}{8} \sqrt{\frac{5}{\pi}} \{ (\overline{ba}_y^4 - \overline{ba}_x^4 + 6\overline{ba}_x^2 \overline{ba}_z^2 - 6\overline{ba}_y^2 \overline{ba}_z^2) (0, 0, 0) + 4(3\overline{ba}_x \overline{ba}_z^2 - \overline{ba}_x^3) (1, 0, 0) \\
& - 4(3\overline{ba}_y \overline{ba}_z^2 - \overline{ba}_y^3) (0, 1, 0) + 12(\overline{ba}_x^2 \overline{ba}_z - \overline{ba}_y^2 \overline{ba}_z) (0, 0, 1) - 6(\overline{ba}_x^2 - \overline{ba}_z^2) \\
& \cdot (2, 0, 0) + 24\overline{ba}_x \overline{ba}_z (1, 0, 1) + 6(\overline{ba}_y^2 - \overline{ba}_z^2) (0, 2, 0) - 24\overline{ba}_y \overline{ba}_z (0, 1, 1) \\
& + 6(\overline{ba}_x^2 - \overline{ba}_y^2) (0, 0, 2) + 4\overline{ba}_x [3(1, 0, 2) - (3, 0, 0)] + 12\overline{ba}_z [(2, 0, 1) - (0, 2, 1)] \\
& + 4\overline{ba}_y [(0, 3, 0) - 3(0, 1, 2)] - (4, 0, 0) + 6(2, 0, 2) + (0, 4, 0) - 6(0, 2, 2) \} \\
& \quad \quad \quad (2.38)
\end{aligned}$$

$$\begin{aligned}
g_{xyz^2} = & \frac{3}{4} \sqrt{\frac{5}{\pi}} \{ (6\overline{ba}_x \overline{ba}_y \overline{ba}_z^2 - \overline{ba}_x^3 \overline{ba}_y - \overline{ba}_x \overline{ba}_y^3) (0, 0, 0) + (6\overline{ba}_y \overline{ba}_z^2 - 3\overline{ba}_x^2 \overline{ba}_y - \overline{ba}_y^3) \\
& \cdot (1, 0, 0) + (6\overline{ba}_x \overline{ba}_z^2 - \overline{ba}_x^3 - 3\overline{ba}_x \overline{ba}_y^2) (0, 1, 0) + 12\overline{ba}_x \overline{ba}_y \overline{ba}_z (0, 0, 1) \\
& + 3(2\overline{ba}_z^2 - \overline{ba}_x^2 - \overline{ba}_y^2) (1, 1, 0) - 3\overline{ba}_x \overline{ba}_y [(2, 0, 0) + (0, 2, 0) - 2(0, 0, 2)] \\
& + 12\overline{ba}_y \overline{ba}_z (1, 0, 1) + 12\overline{ba}_x \overline{ba}_z (0, 1, 1) - \overline{ba}_y [(3, 0, 0) + 3(1, 2, 0) - 6(1, 0, 2)] \\
& - \overline{ba}_x [3(2, 1, 0) + (0, 3, 0) - 6(0, 1, 2)] + 12\overline{ba}_z (1, 1, 1) - (3, 1, 0) - (1, 3, 0) \\
& + 6(1, 1, 2) \} \\
& \quad \quad \quad (2.39)
\end{aligned}$$

$$\begin{aligned}
g_{z(x^3-3xy^2)} &= \frac{3}{8} \sqrt{\frac{70}{\pi}} \{ (\overline{ba_x^3} \overline{ba_z} - 3 \overline{ba_x} \overline{ba_y^2} \overline{ba_z}) (0, 0, 0) + 3 (\overline{ba_x^2} \overline{ba_z} - \overline{ba_y^2} \overline{ba_z}) (1, 0, 0) \\
&\quad - 6 \overline{ba_x} \overline{ba_y} \overline{ba_z} (0, 1, 0) + (\overline{ba_x^3} - 3 \overline{ba_x} \overline{ba_y^2}) (0, 0, 1) - 6 \overline{ba_y} \overline{ba_z} (1, 1, 0) \\
&\quad + 3 \overline{ba_x} \overline{ba_z} [(2, 0, 0) - (0, 2, 0)] + 3 (\overline{ba_x^2} - \overline{ba_y^2}) (1, 0, 1) - 6 \overline{ba_x} \overline{ba_y} (0, 1, 1) \\
&\quad + \overline{ba_z} [(3, 0, 0) - 3(1, 2, 0)] + 3 \overline{ba_x} [(2, 0, 1) - (0, 2, 1)] - 6 \overline{ba_y} (1, 1, 1) \\
&\quad + (3, 0, 1) - 3(1, 2, 1) \}
\end{aligned} \tag{2.40}$$

$$\begin{aligned}
g_{z(3x^2y-y^3)} &= \frac{3}{8} \sqrt{\frac{70}{\pi}} \{ (3 \overline{ba_x^2} \overline{ba_y} \overline{ba_z} - \overline{ba_y^3} \overline{ba_z}) (0, 0, 0) + 3 (\overline{ba_x^2} \overline{ba_z} - \overline{ba_y^2} \overline{ba_z}) (0, 1, 0) \\
&\quad + 6 \overline{ba_x} \overline{ba_y} \overline{ba_z} (1, 0, 0) + (3 \overline{ba_x^2} \overline{ba_y} - \overline{ba_y^3}) (0, 0, 1) + 6 \overline{ba_x} \overline{ba_z} (1, 1, 0) \\
&\quad + 3 \overline{ba_y} \overline{ba_z} [(2, 0, 0) - (0, 2, 0)] + 3 (\overline{ba_x^2} - \overline{ba_y^2}) (0, 1, 1) - 6 \overline{ba_x} \overline{ba_y} (1, 0, 1) \\
&\quad + \overline{ba_z} [3(2, 1, 0) - (0, 3, 0)] + 3 \overline{ba_y} [(2, 0, 1) - (0, 2, 1)] + 6 \overline{ba_x} (1, 1, 1) \\
&\quad - (0, 3, 1) + 3(2, 1, 1) \}
\end{aligned} \tag{2.41}$$

$$\begin{aligned}
g_{x^2y^2} = & \frac{3}{16} \sqrt{\frac{35}{\pi}} \{ (\overline{ba_x^4} - 6\overline{ba_x^2ba_y^2} + \overline{ba_y^4})(0,0,0) + 4(\overline{ba_x^3} - 3\overline{ba_xba_y^2})(1,0,0) \\
& + 4(\overline{ba_y^3} - 3\overline{ba_x^2ba_y})(0,1,0) + 6(\overline{ba_x^2} - \overline{ba_y^2})[(2,0,0) - (0,2,0)] - 24\overline{ba_xba_y}(1,1,0) \\
& + 4\overline{ba_x}[(3,0,0) - 3(1,2,0)] + 4\overline{ba_y}[(0,3,0) - 3(2,1,0)] + (4,0,0) - 6(2,2,0) \\
& + (0,4,0) \}
\end{aligned} \tag{2.42}$$

$$\begin{aligned}
g_{xy(x^2-y^2)} = & \frac{3}{4} \sqrt{\frac{35}{\pi}} \{ (\overline{ba_x^3ba_y} - \overline{ba_xba_y^3})(0,0,0) + (3\overline{ba_x^2ba_y} - \overline{ba_y^3})(1,0,0) + \\
& (\overline{ba_x^3} - 3\overline{ba_xba_y^2})(0,1,0) + 3\overline{ba_xba_y}[(2,0,0) - (0,2,0)] + 3(\overline{ba_x^2} - \overline{ba_y^2})(1,1,0) \\
& + \overline{ba_y}[(3,0,0) - 3(1,2,0)] + \overline{ba_x}[3(2,1,0) - (0,3,0)] + (3,1,0) - (1,3,0) \}
\end{aligned} \tag{2.43}$$

Master formulas for operator translation:

$$\begin{aligned}
(n, l, m)^O &= \sum_{\nu} f_{\nu}^o(\overline{bo_x}, \overline{bo_y}, \overline{bo_z})(i, j, k)_{\nu}^B \\
(1, 0, 0) &= \overline{bo_x}(0, 0, 0) + (1, 0, 0) \\
(0, 1, 0) &= \overline{bo_y}(0, 0, 0) + (0, 1, 0) \\
(0, 0, 1) &= \overline{bo_z}(0, 0, 0) + (0, 0, 1) \\
(2, 0, 0) &= \overline{bo_x^2}(0, 0, 0) + 2\overline{bo_x}(1, 0, 0) + (2, 0, 0) \\
(1, 1, 0) &= \overline{bo_xbo_y}(0, 0, 0) + \overline{bo_y}(1, 0, 0) + \overline{bo_x}(0, 1, 0) + (1, 1, 0)
\end{aligned}$$

$$(1, 0, 1) = \overline{bo_x}\overline{bo_z}(0, 0, 0) + \overline{bo_z}(1, 0, 0) + \overline{bo_x}(0, 0, 1) + (1, 0, 1)$$

$$(0, 2, 0) = \overline{bo_y}^2(0, 0, 0) + 2\overline{bo_y}(0, 1, 0) + (0, 2, 0)$$

$$(0, 1, 1) = \overline{bo_y}\overline{bo_z}(0, 0, 0) + \overline{bo_z}(0, 1, 0) + \overline{bo_y}(0, 0, 1) + (0, 1, 1)$$

$$(0, 0, 2) = \overline{bo_z}^2(0, 0, 0) + 2\overline{bo_z}(0, 0, 1) + (0, 0, 2)$$

$$(3, 0, 0) = \overline{bo_x}^3(0, 0, 0) + 3\overline{bo_x}^2(1, 0, 0) + 3\overline{bo_x}(2, 0, 0) + (3, 0, 0)$$

$$(1, 2, 0) = \overline{bo_x}\overline{bo_y}^2(0, 0, 0) + \overline{bo_y}^2(1, 0, 0) + 2\overline{bo_x}\overline{bo_y}(0, 1, 0) + 2\overline{bo_y}(1, 1, 0)$$

$$+ \overline{bo_x}(0, 2, 0) + (1, 2, 0)$$

$$(1, 0, 2) = \overline{bo_x}\overline{bo_z}^2(0, 0, 0) + \overline{bo_z}^2(1, 0, 0) + 2\overline{bo_x}\overline{bo_z}(0, 0, 1) + 2\overline{bo_z}(1, 0, 1)$$

$$+ \overline{bo_x}(0, 0, 2) + (1, 0, 2)$$

$$(2, 1, 0) = \overline{bo_x}^2\overline{bo_y}(0, 0, 0) + 2\overline{bo_x}\overline{bo_y}(1, 0, 0) + \overline{bo_x}^2(0, 1, 0) + 2\overline{bo_x}(1, 1, 0)$$

$$+ \overline{bo_y}(2, 0, 0) + (2, 1, 0)$$

$$(2, 0, 1) = \overline{bo_x}^2\overline{bo_z}(0, 0, 0) + 2\overline{bo_x}\overline{bo_z}(1, 0, 0) + \overline{bo_x}^2(0, 0, 1) + 2\overline{bo_x}(1, 0, 1)$$

$$+ \overline{bo_z}(2, 0, 0) + (2, 0, 1)$$

$$(1, 1, 1) = \overline{bo_x}\overline{bo_y}\overline{bo_z}(0, 0, 0) + \overline{bo_y}\overline{bo_z}(1, 0, 0) + \overline{bo_x}\overline{bo_z}(0, 1, 0) + \overline{bo_x}\overline{bo_y}(0, 0, 1)$$

$$+ \overline{bo_z}(1, 1, 0) + \overline{bo_y}(1, 0, 1) + \overline{bo_x}(0, 1, 1) + (1, 1, 1)$$

$$(0, 3, 0) = \overline{bo_y}^3(0, 0, 0) + 3\overline{bo_y}^2(0, 1, 0) + 3\overline{bo_y}(0, 2, 0) + (0, 3, 0)$$

$$(0, 1, 2) = \overline{bo_y}\overline{bo_z}^2(0, 0, 0) + \overline{bo_z}^2(0, 1, 0) + 2\overline{bo_y}\overline{bo_z}(0, 0, 1) + 2\overline{bo_z}(0, 1, 1)$$

$$+ \overline{bo_y}(0, 0, 2) + (0, 1, 2)$$

$$(0, 2, 1) = \overline{bo_y}^2\overline{bo_z}(0, 0, 0) + 2\overline{bo_y}\overline{bo_z}(0, 1, 0) + \overline{bo_y}^2(0, 0, 1) + 2\overline{bo_y}(0, 1, 1)$$

$$+ \overline{bo_z}(0, 2, 0) + (0, 2, 1)$$

$$(0, 0, 3) = \overline{bo_z}^3(0, 0, 0) + 3\overline{bo_z}^2(0, 0, 1) + 3\overline{bo_z}(0, 0, 2) + (0, 0, 3)$$

$$(4, 0, 0) = \overline{bo_x}^4(0, 0, 0) + 4\overline{bo_x}^3(1, 0, 0) + 6\overline{bo_x}^2(2, 0, 0) + 4\overline{bo_x}(3, 0, 0) + (4, 0, 0)$$

$$\begin{aligned}
(3, 1, 0) &= \overline{bo}_x^3 \overline{bo}_y(0, 0, 0) + 3\overline{bo}_x^2 \overline{bo}_y(1, 0, 0) + \overline{bo}_x^3(0, 1, 0) + 3\overline{bo}_x \overline{bo}_y(2, 0, 0) \\
&\quad + 3\overline{bo}_x^2(1, 1, 0) + \overline{bo}_y(3, 0, 0) + 3\overline{bo}_x(2, 1, 0) + (3, 1, 0) \\
(3, 0, 1) &= \overline{bo}_x^3 \overline{bo}_z(0, 0, 0) + 3\overline{bo}_x^2 \overline{bo}_z(1, 0, 0) + \overline{bo}_x^3(0, 0, 1) + 3\overline{bo}_x^2(1, 0, 1) \\
&\quad + 3\overline{bo}_x \overline{bo}_z(2, 0, 0) + \overline{bo}_z(3, 0, 0) + 3\overline{bo}_x(2, 0, 1) + (3, 0, 1) \\
(2, 2, 0) &= \overline{bo}_x^2 \overline{bo}_y^2(0, 0, 0) + 2\overline{bo}_x \overline{bo}_y^2(1, 0, 0) + 2\overline{bo}_x^2 \overline{bo}_y(0, 1, 0) + \overline{bo}_y^2(2, 0, 0) \\
&\quad + 4\overline{bo}_x \overline{bo}_y(1, 1, 0) + \overline{bo}_x^2(0, 2, 0) + 2\overline{bo}_x(1, 2, 0) + 2\overline{bo}_y(2, 1, 0) + (2, 2, 0) \\
(2, 1, 1) &= \overline{bo}_x^2 \overline{bo}_y \overline{bo}_z(0, 0, 0) + 2\overline{bo}_x \overline{bo}_y \overline{bo}_z(1, 0, 0) + \overline{bo}_x^2 \overline{bo}_z(0, 1, 0) + \overline{bo}_x^2 \overline{bo}_y(0, 0, 1) \\
&\quad + \overline{bo}_y \overline{bo}_z(2, 0, 0) + 2\overline{bo}_x \overline{bo}_z(1, 1, 0) + 2\overline{bo}_x \overline{bo}_y(1, 0, 1) + \overline{bo}_x^2(0, 1, 1) \\
&\quad + \overline{bo}_z(2, 1, 0) + \overline{bo}_y(2, 0, 1) + 2\overline{bo}_x(1, 1, 1) + (2, 1, 1) \\
(2, 0, 2) &= \overline{bo}_x^2 \overline{bo}_z^2(0, 0, 0) + 2\overline{bo}_x \overline{bo}_z^2(1, 0, 0) + 2\overline{bo}_x^2 \overline{bo}_z(0, 0, 1) + 4\overline{bo}_x \overline{bo}_z(1, 0, 1) \\
&\quad + \overline{bo}_z^2(2, 0, 0) + \overline{bo}_x^2(0, 0, 2) + 2\overline{bo}_x(1, 0, 2) + 2\overline{bo}_z(2, 0, 1) + (2, 0, 2) \\
(1, 3, 0) &= \overline{bo}_x \overline{bo}_y^3(0, 0, 0) + 3\overline{bo}_x \overline{bo}_y^2(0, 1, 0) + \overline{bo}_y^3(1, 0, 0) + 3\overline{bo}_x \overline{bo}_y(0, 2, 0) \\
&\quad + 3\overline{bo}_y^2(1, 1, 0) + \overline{bo}_x(0, 3, 0) + 3\overline{bo}_y(1, 2, 0) + (1, 3, 0) \\
(1, 2, 1) &= \overline{bo}_x \overline{bo}_y^2 \overline{bo}_z(0, 0, 0) + 2\overline{bo}_x \overline{bo}_y \overline{bo}_z(0, 1, 0) + \overline{bo}_y^2 \overline{bo}_z(1, 0, 0) + \overline{bo}_x \overline{bo}_y^2(0, 0, 1) \\
&\quad + \overline{bo}_x \overline{bo}_z(0, 2, 0) + 2\overline{bo}_y \overline{bo}_z(1, 1, 0) + 2\overline{bo}_x \overline{bo}_y(0, 1, 1) + \overline{bo}_y^2(1, 0, 1) \\
&\quad + \overline{bo}_z(1, 2, 0) + \overline{bo}_x(0, 2, 1) + 2\overline{bo}_y(1, 1, 1) + (1, 2, 1) \\
(1, 1, 2) &= \overline{bo}_x \overline{bo}_y \overline{bo}_z^2(0, 0, 0) + \overline{bo}_y \overline{bo}_z^2(1, 0, 0) + \overline{bo}_x \overline{bo}_z^2(0, 1, 0) + 2\overline{bo}_x \overline{bo}_y \overline{bo}_z(0, 0, 1) \\
&\quad + \overline{bo}_z^2(1, 1, 0) + 2\overline{bo}_y \overline{bo}_z(1, 0, 1) + 2\overline{bo}_x \overline{bo}_z(0, 1, 1) + \overline{bo}_x \overline{bo}_y(0, 0, 2) \\
&\quad + \overline{bo}_y(1, 0, 2) + 2\overline{bo}_z(1, 1, 1) + \overline{bo}_x(0, 1, 2) + (1, 1, 2) \\
(1, 0, 3) &= \overline{bo}_x \overline{bo}_z^3(0, 0, 0) + \overline{bo}_z^3(1, 0, 0) + 3\overline{bo}_x \overline{bo}_z^2(0, 0, 1) + 3\overline{bo}_z^2(1, 0, 1) \\
&\quad + 3\overline{bo}_x \overline{bo}_z(0, 0, 2) + 3\overline{bo}_z(1, 0, 2) + \overline{bo}_x(0, 0, 3) + (1, 0, 3)
\end{aligned}$$

$$\begin{aligned}
(0, 4, 0) &= \overline{bo}_y^4(0, 0, 0) + 4\overline{bo}_y^3(0, 1, 0) + 6\overline{bo}_y^2(0, 2, 0) + 4\overline{bo}_y(0, 3, 0) + (0, 4, 0) \\
(0, 3, 1) &= \overline{bo}_y^3\overline{bo}_z(0, 0, 0) + 3\overline{bo}_y^2\overline{bo}_z(0, 1, 0) + \overline{bo}_y^3(0, 0, 1) + 3\overline{bo}_y^2(0, 1, 1) \\
&\quad + 3\overline{bo}_x\overline{bo}_z(0, 2, 0) + \overline{bo}_z(0, 3, 0) + 3\overline{bo}_y(0, 2, 1) + (0, 3, 1) \\
(0, 2, 2) &= \overline{bo}_y^2\overline{bo}_z^2(0, 0, 0) + 2\overline{bo}_y\overline{bo}_z^2(0, 1, 0) + 2\overline{bo}_y^2\overline{bo}_z(0, 0, 1) + 4\overline{bo}_y\overline{bo}_z(0, 1, 1) \\
&\quad + \overline{bo}_z^2(0, 2, 0) + \overline{bo}_y^2(0, 0, 2) + 2\overline{bo}_y(0, 1, 2) + 2\overline{bo}_z(0, 2, 1) + (0, 2, 2) \\
(0, 1, 3) &= \overline{bo}_y\overline{bo}_z^3(0, 0, 0) + \overline{bo}_z^3(0, 1, 0) + 3\overline{bo}_y\overline{bo}_z^2(0, 0, 1) + 3\overline{bo}_z^2(0, 1, 1) \\
&\quad + 3\overline{bo}_y\overline{bo}_z(0, 0, 2) + 3\overline{bo}_z(0, 1, 2) + \overline{bo}_y(0, 0, 3) + (0, 1, 3) \\
(0, 0, 4) &= \overline{bo}_z^4(0, 0, 0) + 4\overline{bo}_z^3(1, 0, 0) + 6\overline{bo}_z^2(0, 0, 2) + 4\overline{bo}_z(0, 0, 3) + (0, 0, 4)
\end{aligned}$$

With this accomplishment we can now write the sixfold sum of equation (2.18) in terms of a twofold sum over the two Cartesians, both centered on B, in the following fashion,

$$\begin{aligned}
\langle M_{l,m,n} \rangle &= \langle r_a^{n_a-l_a-1} x_a^i y_a^j z_a^k e^{-\zeta_a r_a} | x_o^l y_o^m z_o^n | r_b^{n_b-l_b-1} x_b^e y_b^f z_b^g e^{-\zeta_b r_b} \rangle \\
&\quad \langle r_a^{n_a-l_a-1} \left(\sum_u g_\mu^a(\overline{ba}_x, \overline{ba}_y, \overline{ba}_z) x_b^{t_{x,u}^a} y_b^{t_{y,u}^a} z_b^{t_{z,u}^a} \right) e^{-\zeta_a r_a} | \\
&\quad \cdot \left(\sum_v f_v^o(\overline{bo}_x, \overline{bo}_y, \overline{bo}_z) x_b^{t_{x,v}^o} y_b^{t_{y,v}^o} z_b^{t_{z,v}^o} \right) | r_b^{n_b-l_b-1} x_b^e y_b^f z_b^g e^{-\zeta_b r_b} \rangle \quad (2.44) \\
&= \sum_{u,v} g_\mu^a(\overline{ba}_x, \overline{ba}_y, \overline{ba}_z) f_v^o(\overline{bo}_x, \overline{bo}_y, \overline{bo}_z) \\
&\quad \cdot \langle r_a^{n_a-l_a-1} e^{-\zeta_a r_a} | r_b^{n_b-l_b-1} x_b^{e+t_{x,u}^a+t_{x,v}^o} y_b^{f+t_{y,u}^a+t_{y,v}^o} z_b^{g+t_{z,u}^a+t_{z,v}^o} e^{-\zeta_b r_b} \rangle
\end{aligned}$$

where the coefficients $g_\mu^a(\overline{ba}_x, \overline{ba}_y, \overline{ba}_z)$ and $f_v^b(\overline{bo}_x, \overline{bo}_y, \overline{bo}_z)$ are taken from the master formulas through two computational do loops.

Local Integral Evaluation

One-center Integrals

After the translations described by equation (2.44), all one-center integrals, apart from a normalization factor, take the form

$$\begin{aligned}
 I_1 &= \langle r_b^{n_a+n_b-l_a-l_b-2} x_b^i y_b^j z_b^k e^{-(\zeta_a+\zeta_b)r_b} \rangle \\
 &= \int_0^\infty r_b^{n_a+n_b-l_a-l_b+i+j+k} e^{-(\zeta_a+\zeta_b)r_b} dr_b \int_0^\pi \sin^{i+j+1}\theta_b \cos^k\theta_b d\theta_b \\
 &\quad \cdot \int_0^{2\pi} \sin^i\phi \cos^j\phi d\phi
 \end{aligned} \tag{2.45}$$

and we proceed to evaluate the non-vanishing angular part of I_1 first.

Assuming m and n to be integers, we have, in general

$$\int_0^{\pi,2\pi} \cos^m\phi \sin^n\phi d\phi = \frac{m-1}{m+n} \int_0^{\pi,2\pi} \cos^{m-2}\phi \sin^n\phi d\phi \tag{2.46}$$

applying equation (2.46) in a recursive manner, we get

$$\begin{aligned}
 \int_0^{\pi,2\pi} \cos^m\phi \sin^n\phi d\phi &= \frac{m-1}{m+n} \cdot \frac{m-3}{m+n-2} \int_0^{\pi,2\pi} \cos^{m-4}\phi \sin^n\phi d\phi \\
 &= \frac{m-1}{m+n} \cdot \frac{m-3}{m+n-2} \cdot \frac{m-5}{m+n-4} \int_0^{\pi,2\pi} \cos^{m-6}\phi \sin^n\phi d\phi = \dots \\
 &= \frac{(m-1)!!n!!}{(m+n)!!} \int_0^{\pi,2\pi} \sin^n\phi d\phi
 \end{aligned} \tag{2.47}$$

In equation (2.47) we need to examine two cases of the sine integral. First, if the

n is even,

$$\begin{aligned} \int_0^{\pi, 2\pi} \sin^n \phi d\phi &= \frac{n-1}{n} \int_0^{\pi, 2\pi} \sin^{n-2} \phi d\phi = \frac{n-1}{n} \cdot \frac{n-3}{n-2} \int_0^{\pi, 2\pi} \sin^{n-4} \phi d\phi = \dots \\ &= \frac{(n-1)!!}{n!!} (\pi, 2\pi) \end{aligned} \quad (2.48)$$

Therefore for even m and even n , equations (2.47) and (2.48) give a closed formulae,

$$\int_0^{\pi} \cos^m \phi \sin^n \phi d\phi = \frac{(m-1)!!(n-1)!!\pi}{(m+n)!!} \quad (2.49)$$

$$\int_0^{2\pi} \cos^m \phi \sin^n \phi d\phi = \frac{(m-1)!!(n-1)!!}{(m+n)!!} (2\pi) = F(m, n) \quad (2.50)$$

We then examine the sine integrals with odd n in equation (2.47),

$$\int_0^{\pi} \sin^n \phi d\phi = -\cos \phi \frac{2^{2(\frac{n-1}{2})} (\frac{n-1}{2})! (\frac{n-1}{2})!}{n!} \Big|_0^{\pi} = \frac{2^n (\frac{n-1}{2})! (\frac{n-1}{2})!}{n!} \quad (2.51)$$

$$\int_0^{2\pi} \sin^n \phi d\phi = 0 \quad (2.52)$$

and finally equations (2.47) and (2.51) give, for even m and odd n , the closed formulae

$$\int_0^{\pi} \cos^m \phi \sin^n \phi d\phi = \frac{(m-1)!!(n-1)!!}{(m+n)!!} \cdot \frac{2^n (\frac{n-1}{2})! (\frac{n-1}{2})!}{n!} \quad (2.53)$$

All the angular integrals necessary for I_1 are given by equations (2.51) and (2.53).

The radial part of I_1 is simply

$$\int_0^{\infty} r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}} \quad (2.54)$$

Two-center Integrals

In an ellipsoidal coordinate system we use equation ((6)) noted previously to express a two-center integral that evolves from the translation of equation (2.44),

$$\begin{aligned}
 I_2 &= \langle r_a^{n_a-l_a-1} e^{-\zeta_a r_a} | r_b^{n_b-l_b-1} x_b^i y_b^j z_b^k e^{\zeta_b r_b} \rangle \\
 &= \int_1^\infty d\xi \int_{-1}^1 d\eta \int_0^{2\pi} d\phi \left(\frac{R}{2}\right)^{n_a+n_b-l_a-l_b+i+j+k+1} (\xi + \eta)^{n_a+1} (\xi - \eta)^{n_b+1} \\
 &\quad \cdot [(\xi^2 - 1)(1 - \eta^2)]^{\frac{1}{2}(i+j)} (1 - \xi\eta)^k e^{-\rho\xi - \tau\rho\eta} \cos^i \phi \sin^j \phi \\
 &= \int_1^\infty d\xi \int_{-1}^1 d\eta \left(\frac{R}{2}\right)^{n_a+n_b-l_a-l_b+i+j+k+1} (\xi + \eta)^{n_a+1} (\xi - \eta)^{n_b+1} \\
 &\quad \cdot [(\xi^2 - 1)(1 - \eta^2)]^{\frac{1}{2}(i+j)} (1 - \xi\eta)^k e^{-\rho\xi - \tau\rho\eta} \cdot F(i, j)
 \end{aligned} \tag{2.55}$$

where

$$\begin{aligned}
 \rho &= \frac{R}{2}(\zeta_a + \zeta_b) \\
 \tau &= \frac{(\zeta_a - \zeta_b)}{(\zeta_a + \zeta_b)}
 \end{aligned} \tag{2.56}$$

and $F(i, j)$ is given by equation (2.50).

At this point we feel it is convenient if a new function is introduced as

$$Z_{\alpha, \beta, \gamma, \delta}(\rho, \tau) = \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi + \eta)^\alpha (\xi - \eta)^\beta [(\xi^2 - 1)(1 - \eta^2)]^\gamma (1 - \xi\eta)^\delta e^{-\rho\xi - \tau\rho\eta} \tag{2.57}$$

which we shall call “Z functions”. The recursion formulas of Z are simpler than those derived by Ruedenberg, Roothaan and Jaunzemis [27]. In this work we adapt an algorithm

proposed by Stevens [59, 60] based on the binomial theorem,

$$Z_{\alpha,\beta,\gamma,\delta}(\rho, \tau) = \sum_{i,j,k,l,m} \binom{\alpha}{i} \binom{\beta}{j} \binom{\gamma}{k} \binom{\gamma}{l} \binom{\delta}{m} (-)^{j+k+l+m} \cdot A_{\alpha+\beta+2\gamma-i-j-2k+m}(\rho) B_{i+j+2l+m}(\rho, \tau) \quad (2.58)$$

where the A and B functions are as defined by Mulliken, Rieke, Orloff and Orloff [61], and have been well studied by, among others, Miller, Gerhauser, Matsen, and Harris [62].

In this formalism, the two-center integral of equation (2.55) is evaluated as the product of Z and F functions,

$$I_2 = \langle r_a^{n_a-l_a-1} e^{-\zeta_a r_a} | r_b^{n_b-l_b-1} x_b^i y_b^j z_b^k e^{\zeta_b r_b} \rangle \quad (2.59)$$

$$= Z_{n_a-l_a, n_b-l_b, (i+j)/2, k}(\rho, \tau) F(i, j)$$

Rotational transform into Molecular Frame

As discussed in section II.3, all integrals evaluated in section III.2 need to be back transformed into the molecular frame $[x', y', z']$ (see Figure 1) through a matrix rotation

$$R(\theta, \phi) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & 0 & r_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \quad (2.60)$$

where the matrix elements are given by equation ((10)). We now let the rotation described by equation (2.60) act on an arbitrary Cartesian in the ellipsoidal coordinate system,

$$R x^i y^j z^k = (r_{11}x + r_{12}y + r_{13}z)^i (r_{21}x + r_{22}y + r_{23}z)^j (r_{31}x + r_{33}z)^k$$

$$= \sum_{(r,s,t)(u,v,w)(p,q)} c_{r,s,t}^i(r_{11}, r_{12}, r_{13}) c_{u,v,w}^j(r_{21}, r_{22}, r_{23}) c_{p,q}^k(r_{31}, r_{33}) \quad (2.61)$$

$$\cdot x^{r+u+p} y^{s+v} z^{t+w+q}$$

where

$$\begin{aligned}
 c_{r,s,t}^i(r_{11}, r_{12}, r_{13}) &= \frac{i!}{r!s!t!} r_{11}^r r_{12}^s r_{13}^t \\
 c_{u,v,w}^j(r_{21}, r_{22}, r_{23}) &= \frac{j!}{u!v!w!} r_{21}^u r_{22}^v r_{23}^w \\
 c_{p,q}^k(r_{31}, r_{33}) &= \frac{k!}{p!q!} r_{31}^p r_{33}^q
 \end{aligned} \tag{2.62}$$

Considering I_2 of equation (2.55), we now have

$$\begin{aligned}
 RI_2 &= R \langle r_a^{n_a} e^{-\zeta_a r_a} | r_b^{n_b} x_b^i y_b^j z_b^k e^{-r_b \zeta_b} \rangle \\
 &= \langle r_a^{n_a} e^{-\zeta_a r_a} | r_b^{n_b} (R x_b^i y_b^j z_b^k) e^{-r_b \zeta_b} \rangle \\
 &= \sum_{(r,s,t)(u,v,w)(p,q)} c_{r,s,t}^i c_{u,v,w}^j c_{p,q}^k \langle r_a^{n_a} e^{-\zeta_a r_a} | r_b^{n_b} x_b^{r+u+p} y_b^{s+v} z_b^{t+w+q} e^{-r_b \zeta_b} \rangle
 \end{aligned} \tag{2.63}$$

where we have applied equation (2.61) and used the rotational equivalence of coordinate systems $[x, y, z]$ and $[x_b, y_b, z_b]$ (see again, Figure 1).

In this approach it is notable that the rotation $R(\theta, \phi)$ needs to act only on the right-hand side of equation (2.55) to rotate the integral I_2 into the molecular frame.

Computational Procedure

The method presented here proceeds as follows:

- i) For two orbitals on the same center the operator is translated, the symmetry is checked, and if non-zero, integral evaluation proceeds as outlined two subsections ago.

ii) For orbitals on different centers:

- (1) Choose the orbital with bigger l in equation (2.3) to be centered on B.
- (2) Translation is made in two do loops of equation (2.44) by using the master formulas.
- (3) Determine the order $L = e + f + g + t_{x,u}^a + t_{x,v}^o + t_{y,u}^a + t_{y,v}^o + t_{z,u}^a + t_{z,v}^o$ of the Cartesian on the right hand side of equation (2.44).
- (4) Sort out the angular symmetry “allowed” Cartesians of the order L determined in step (3) by way of the F (i,j) functions shown two subsections ago.
- (5) Compute the necessary Z functions [equation (2.58)], and then the local integrals [equation (2.59)] required by step (4).
- (6) Rotate the computed local integrals into the molecular frame by using equation (2.63).

Based on this procedure, a program package HIMO is produced based on a flow chart shown in Figure 1.

Discussion and Conclusions

A general method of evaluating electric moment integrals over Slater-type orbitals is developed. A program that implements the procedure described in the last section has been in use in this laboratory for some time. We have been using these moments for

studies on solvation using the self-consistent reaction field model, and for examining the long-range interactions between molecules.

The method we outline is somewhat unusual in that the Cartesian components of one orbital and the operator are both translated to the center of another orbital and thus only a single sigma symmetry integration remains between an s orbital on one center and a complex Cartesian orbital of the form $x^i y^j z^k r^l e^{-\zeta r}$ on the other. The local evaluation of this integral is easy, as is the rotation back into the molecular frame. Although the method is quite general, the price we pay for this computational simplicity is formal complexity. Generating explicit formula for higher moments, or higher angular momentum atomic-like orbitals, is tedious. We do not maintain the “symmetry” of the spherical harmonics and we pay a penalty for this.

A definite advantage of the method described is that we need to consider z component of one atomic orbital, and the Z function we need [equation (2.57)] is simpler than the traditional L function [29],

$$L_{\alpha,\beta}^{\gamma,\delta,\epsilon}(\rho, \tau) = \int_1^\infty d\xi \int_{-1}^1 d\eta (\xi + \eta)^\alpha (\xi - \eta)^\beta (1 + \xi\eta)^\gamma (1 - \xi\eta)^\delta \\ [(\xi^2 - 1)(1 - \eta^2)]^\epsilon e^{-\rho\xi - \tau\rho\eta} \quad (2.64)$$

or the C function [27],

$$C_{\alpha,\beta}^{\gamma,\delta,\epsilon}(\rho, \tau) = \left(\frac{1}{2}\zeta_b R\right)^{\alpha+\beta+\gamma+\delta+2\epsilon+1} L_{\alpha,\beta}^{\gamma,\delta,\epsilon}(\rho, \tau) \quad (2.65)$$

Both L and C functions, if evaluated in the fashion of equation (2.58) require a six-fold sum, while the evaluation of Z functions needs a five-fold sum, a saving of the innermost do loop in computation. It would be worthwhile to further investigate the Z function recursion relations.

Before concluding we further note that the “Cartesian STOs” are prescreened based on angular symmetry before the integration takes place. Note that i and j in the Cartesian (i, j, k) that occurs in equation (2.55) must both be even or the integral vanishes. For example, a typical non-vanishing quadrupole integral between d orbitals contains on average 18 different terms of 64 possible, but only 5 or 6 are non-zero. In Table 2–1 we list the number of Cartesians for a given order, and the number of Cartesians that have non-vanishing angular integral based on the prescreening of $F(i,j)$. This table shows that in the integration with Cartesian STO’s, there is a saving of about 70%.

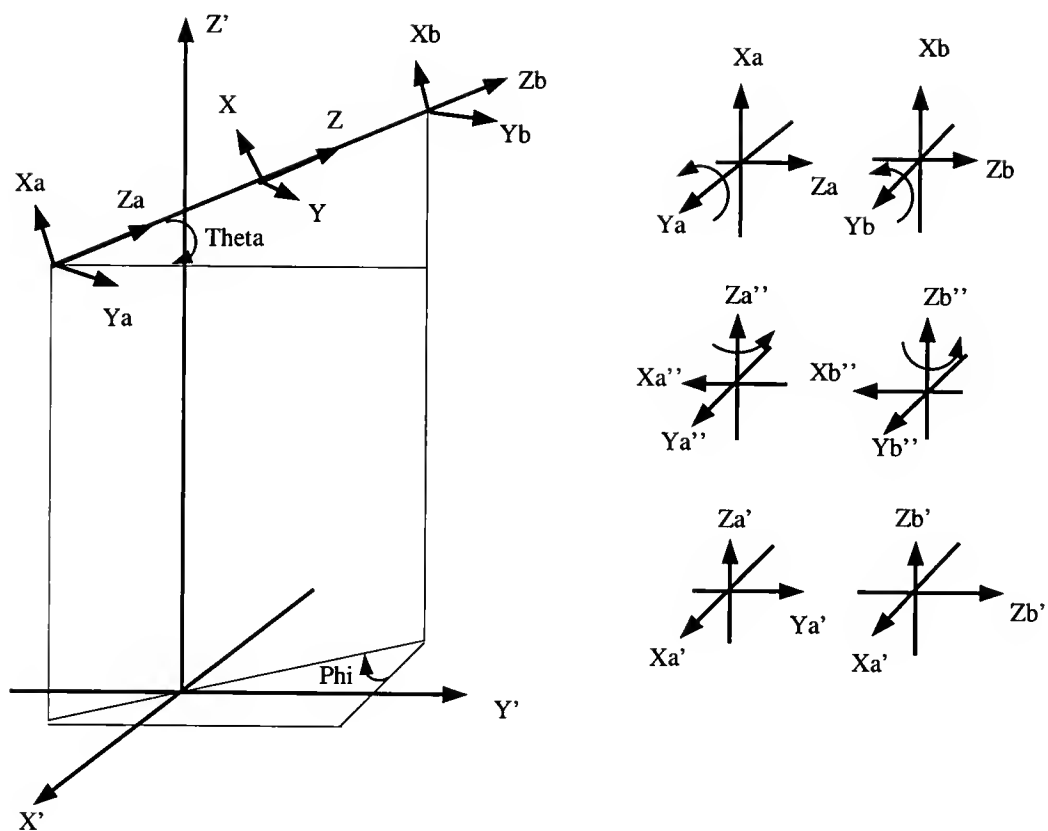


Figure 1: Rotation From Ellipsoidal Coordinate to Molecular Frame

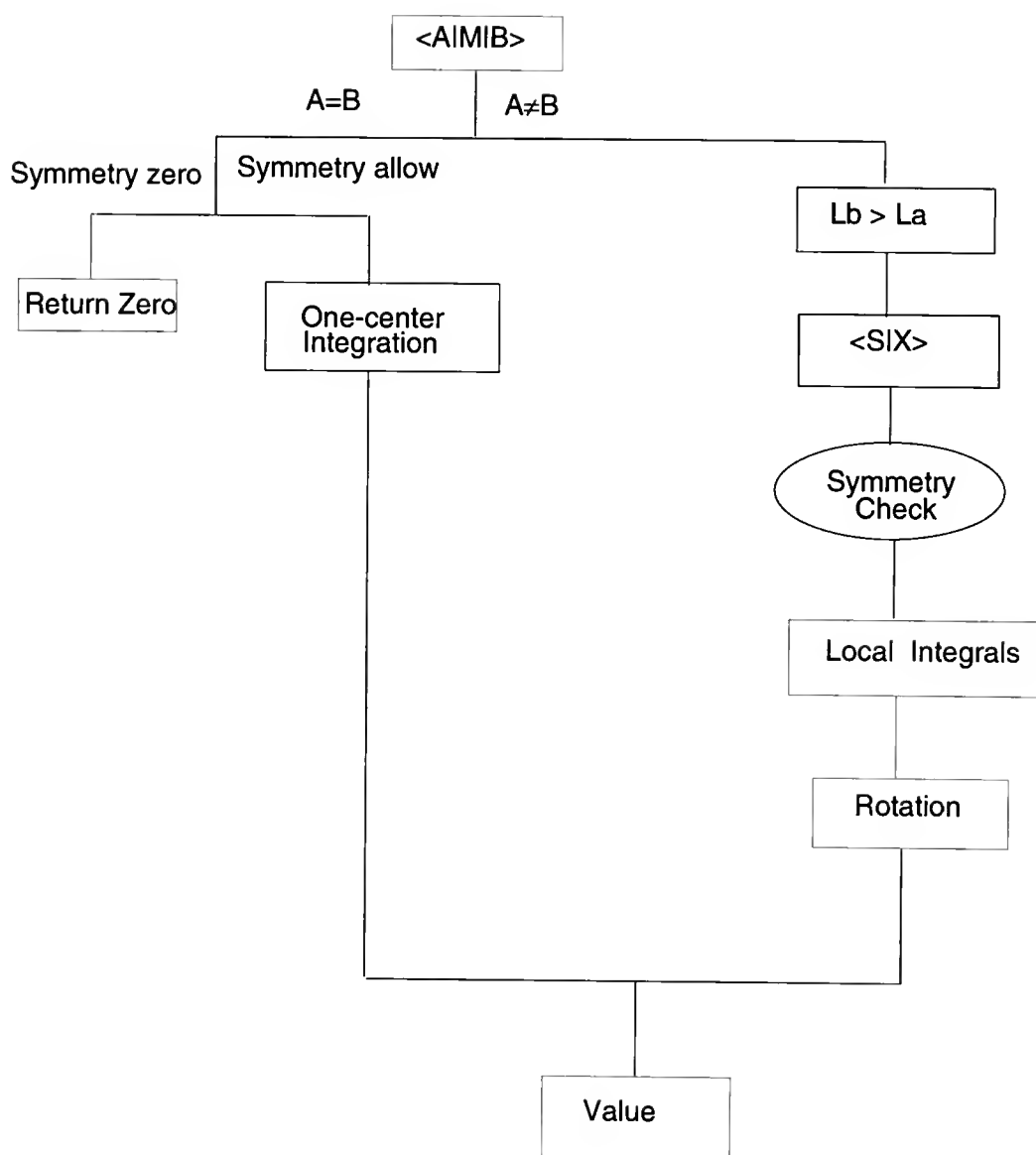


Figure 2: Flow chart of the HIMO computational program

Table 2-1: Percentage of Cartesians needed to Compute

order	Number of Cartesians (A)	Number of Cartesians with Nonzero Angular Integral (B)	B/A
0	1	1	1.00
1	3	1	0.33
2	6	3	0.50
3	10	3	0.30
4	15	6	0.40
5	21	6	0.29
6	28	10	0.36
7	36	10	0.28
8	45	15	0.33
9	55	15	0.27
10	66	21	0.32
11	78	21	0.27
12	91	28	0.31

CHAPTER 3

THE CALCULATION OF MOLECULAR ELECTRIC MULTIPOLE MOMENTS

Definitions of Electric Multipole Moments

There exist many definitions of electric multipole moments in the literature. Very often this situation causes a great deal of confusion in comparing results of different workers, therefore caution must be taken here.

Physicists usually define multipole moments as complex quantities. The potential outside the encompassing sphere of a charge density $\rho(\mathbf{x}')$ can be written as multipole expansion of complex spherical harmonics:

$$\Phi(X) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} q_{l,m} \frac{\bar{Y}_{l,m}(\theta, \phi)}{r^{l+1}} \quad (3.1)$$

and on the other hand Coulomb's law has

$$\Phi(X) = \int \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d^3x' \quad (3.2)$$

. Now applying the Von Neumann expansion to equation (3.2), we can rewrite equation (3.1) as

$$\Phi(X) = 4\pi \sum_{l,m} \frac{1}{2l+1} \left[\int \bar{Y}^*(\theta', \phi') r'^l \rho(\mathbf{x}') d^3x' \right] \frac{\bar{Y}_{l,m}(\theta, \phi)}{r^{l+1}} \quad (3.3)$$

the coefficient of the multipole expansion of equation (3.1) is therefore defined as multipole moments,

$$q_{l,m} = \int \bar{Y}^*(\theta', \phi') r'^l \rho(x') d^3x' \quad (3.4)$$

with the first several multipole moments expressed as follows:

Monopole: $l = 0$

$$q_{0,0} = \frac{1}{\sqrt{4\pi}} \int \rho(x') d^3x' = \frac{1}{\sqrt{4\pi}} q \quad (3.5)$$

where q is the charge of the density distribution; and

Dipole: $l = 1$

$$\begin{aligned} q_{1,1} &= -\sqrt{\frac{3}{8\pi}} \int (x' - iy') \rho(x') d^3x' = -\sqrt{\frac{3}{8\pi}} (p_x - ip_y) \\ q_{1,0} &= \sqrt{\frac{3}{4\pi}} \int z' \rho(x') d^3x' = \sqrt{\frac{3}{4\pi}} p_z \end{aligned} \quad (3.6)$$

where p_i is the i -th dipole component; and

Quadrupole: $l = 2$

$$\begin{aligned} q_{2,2} &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \int (x' - iy')^2 \rho(x') d^3x' = \frac{1}{12} \sqrt{\frac{15}{2\pi}} (Q_{11} - 2iQ_{12} - Q_{22}) \\ q_{2,1} &= \sqrt{\frac{15}{8\pi}} \int z' (x' - iy') \rho(x') d^3x' = -\frac{1}{3} \sqrt{\frac{15}{8\pi}} (Q_{13} - iQ_{23}) \\ q_{2,0} &= \frac{1}{2} \sqrt{\frac{5}{4\pi}} \int (3z'^2 - r'^2) \rho(x') d^3x' = \frac{1}{2} \sqrt{\frac{5}{4\pi}} Q_{33} \end{aligned} \quad (3.7)$$

where Q_{ij} is the quadrupole moment tensor

$$Q_{ij} = \int (3x'_i x'_j - r'^2 \delta_{ij}) \rho(x') d^3x' \quad (3.8)$$

The above type of definition can be found in Jackson [63].

A much simpler definition is given by Bottcher [64], as

Dipole:

$$M = \int x' \rho(x') d^3x' \quad (3.9)$$

Quadrupole:

$$Q = \frac{1}{2!} \int x' x' \rho(x') d^3x' \quad (3.10)$$

Octopole:

$$U = \frac{1}{3!} \int x' x' x' \rho(x') d^3x' \quad (3.11)$$

resulting in an expression of the potential that can be written as

$$\Phi = \frac{q}{r} - M \cdot \nabla \frac{1}{r} + Q : \nabla \nabla \frac{1}{r} - U : \nabla \nabla \nabla \frac{1}{r} + \dots \quad (3.12)$$

Although this set of multipole moments may seem to be overly simple, it has much mathematical convenience when organized in the formation of polytensor in the work of Applequist [65, 66], and subsequently applied to molecular electrical property calculations by Liu, *et al.*[67] and to the electrostatic interaction potential formulation by Dykstra [68].

A third definition is put forth by Buckingham [69], Kielich [70], Stogryn and Stogryn [71], and Krishnaji and Prakash [72]. This definition comes out very naturally from the Taylor series expansion of electrostatic potential of a charge distribution, therefore it is

easy to use in applications and enjoys great popularity among chemists. For convenience we choose Buckingham's definition of multipole moments, and we carefully establish it as follows.

We consider a charge density $\rho(r)$ at point (x, y, z) represented by the vector r from a chosen origin O. The electrostatic potential due to this charge density at an arbitrary point P(X,Y,Z), denoted by a vector R from the origin O, is written as

$$\begin{aligned}\Phi(P) &= \int \frac{\rho(r)}{r'} d^3r \\ &= \int \frac{\rho(r)}{\sqrt{(X-x)^2 + (Y-y)^2 + (Z-z)^2}} d^3r\end{aligned}\quad (3.13)$$

where r' is the vector pointing from (x,y,z) to P(X,Y,Z). In the vicinity of O, where $R > r$, one can expand $\frac{1}{r'}$ in equation (3.13) to achieve

$$\begin{aligned}\Phi(P) &= \int \rho(r) \left[\frac{1}{R} + \left(\frac{\partial(1/r')}{\partial r_\alpha} \right)_0 r_\alpha + \frac{1}{2} \left(\frac{\partial^2(1/r')}{\partial r_\alpha \partial r_\beta} \right)_0 r_\alpha r_\beta + \right. \\ &\quad \left. \frac{1}{6} \left(\frac{\partial^3(1/r')}{\partial r_\alpha \partial r_\beta \partial r_\gamma} \right)_0 r_\alpha r_\beta r_\gamma + \frac{1}{24} \left(\frac{\partial^4(1/r')}{\partial r_\alpha \partial r_\beta \partial r_\gamma \partial r_\delta} \right)_0 r_\alpha r_\beta r_\gamma r_\delta + \dots \right] d^3r \\ &= \int \rho(r) \left\{ \frac{1}{R} + \left(\frac{X}{R} x + \frac{Y}{R} y + \frac{Z}{R} z \right) + \right. \\ &\quad \left. \frac{1}{2} \left[\left(\frac{2X^2 - Y^2 - Z^2}{R^5} \right) x^2 + \left(\frac{2Y^2 - X^2 - Z^2}{R^5} \right) y^2 + \left(\frac{2Z^2 - X^2 - Y^2}{R^5} \right) z^2 + \right. \right. \\ &\quad \left. \frac{6XY}{R^5} xy + \frac{6XZ}{R^5} xz + \frac{6YZ}{R^5} yz \right] + \\ &\quad 9(5X^2Y - YR^2)x^2y + 9(5X^2Z - ZR^2)x^2z + 9(5XY^2 - XR^2)xy^2 + \\ &\quad 9(5XZ^2 - XR^2)xz^2 + 9(5Y^2Z - ZR^2)y^2z + 9(5YZ^2 - YR^2)yz^2 + \\ &\quad \left. 6(XYZ)xyz \right\} d^3r\end{aligned}$$

$$\begin{aligned}
& \frac{1}{24R^9}[(105X^4 - 90X^2R^2 + 9R^4)x^4 + (105Y^4 - 90Y^2R^2 + 9R^4)y^4 + \\
& (105Z^4 - 90Z^2R^2 + 9R^4)z^4 + 4(105X^3Y - 45XYR^2)x^3y + \\
& 4(105X^3Z - 45XZR^2)x^3z + 4(105XY^3 - 45XYR^2)xy^3 + \\
& 4(105XZ^3 - 45XZR^2)xz^3 + 4(105Y^3Z - 45YZR^2)y^3z + \\
& 4(105YZ^3 - 45YZR^2)yz^3 + 6(105X^2Y^2 - 15X^2R^2 - 15Y^2R^2 + 3R^4)x^2y^2 + \\
& 6(105X^2Z^2 - 15X^2R^2 - 15Z^2R^2 + 3R^4)x^2z^2 + \\
& 6(105Y^2Z^2 - 15Y^2R^2 - 15Z^2R^2 + 3R^4)y^2z^2 + \\
& 12(105X^2YZ - 15YZR^2)x^2yz + \\
& 12(105XY^2Z - 15XZR^2)xy^2z + \\
& 12(105XYZ^2 - 15XYR^2)xyz^2] + \dots\}d^3r
\end{aligned} \tag{3.14}$$

To extend equation (3.14) is obviously getting very cumbersome as we proceed to higher orders. Therefore, to prevent the terms from getting intractable, it is convenient to define a set of electric multipole moments in the following fashion,

Monopole:

$$q = \int \rho(r) d^3r \tag{3.15}$$

Dipole:

$$\mu_x = \int x\rho(r) d^3r$$

$$\begin{aligned}
\mu_y &= \int y \rho(r) d^3r \\
\mu_z &= \int z \rho(r) d^3r
\end{aligned} \tag{3.16}$$

Quadrupole:

$$\begin{aligned}
Q_{xx} &= \frac{1}{2} \int (2x^2 - y^2 - z^2) \rho(r) d^3r \\
Q_{yy} &= \frac{1}{2} \int (2y^2 - x^2 - z^2) \rho(r) d^3r \\
Q_{zz} &= \frac{1}{2} \int (2z^2 - x^2 - y^2) \rho(r) d^3r \\
Q_{xy} &= \frac{3}{2} \int xy \rho(r) d^3r \\
Q_{xz} &= \frac{3}{2} \int xz \rho(r) d^3r \\
Q_{yz} &= \frac{3}{2} \int yz \rho(r) d^3r
\end{aligned} \tag{3.17}$$

Octopole:

$$\begin{aligned}
\Omega_{xxx} &= \frac{1}{2} \int (2x^3 - 3xy^2 - 3xz^2) d^3r \\
\Omega_{yyy} &= \frac{1}{2} \int (2y^3 - 3x^2y - 3yz^2) d^3r \\
\Omega_{zzz} &= \frac{1}{2} \int (2z^3 - 3x^2z - 3y^2z) d^3r \\
\Omega_{xxy} &= \frac{1}{2} \int (4x^2y - y^3 - yz^2) \rho(r) d^3r \\
\Omega_{xxz} &= \frac{1}{2} \int (4x^2z - y^2z - z^3) \rho(r) d^3r \\
\Omega_{xyy} &= \frac{1}{2} \int (4xy^2 - x^3 - xz^2) \rho(r) d^3r \\
\Omega_{xyz} &= \frac{5}{2} \int xyz \rho(r) d^3r \\
\Omega_{xzz} &= \frac{1}{2} \int (4xz^2 - x^3 - xy^2) \rho(r) d^3r
\end{aligned}$$

$$\begin{aligned}
\Omega_{yyz} &= \frac{1}{2} \int (4y^2z - x^2z - z^3) \rho(r) d^3r \\
\Omega_{yzz} &= \frac{1}{2} \int (4yz^2 - x^2y - y^3) \rho(r) d^3r
\end{aligned} \tag{3.18}$$

Hexadecapole:

$$\begin{aligned}
\Gamma_{xxxx} &= \int \left[x^4 - 3(x^2y^2 + x^2z^2) + \frac{3}{8}(z^4 + y^4) + \frac{3}{4}y^2z^2 \right] \rho(r) d^3r \\
\Gamma_{xxxy} &= \int \left[\frac{5}{2}x^3y - \frac{15}{8}(xy^3 + xyz^2) \right] \rho(r) d^3r \\
\Gamma_{xxxz} &= \int \left[\frac{5}{2}x^3z - \frac{15}{8}(xy^2z + xz^3) \right] \rho(r) d^3r \\
\Gamma_{xxyy} &= \int \left[\frac{3}{8}(9x^2y^2 - x^2z^2 - y^2z^2) - \frac{1}{2}(x^4 + y^4) + \frac{1}{8}z^4 \right] \rho(r) d^3r \\
\Gamma_{xxyz} &= \int \left[\frac{15}{4}x^2yz - \frac{5}{8}(yz^3 + y^3z) \right] \rho(r) d^3r \\
\Gamma_{xxzz} &= \int \left[\frac{3}{8}(9x^2z^2 - x^2y^2 - y^2z^2) - \frac{1}{2}(z^4 + x^4) + \frac{1}{8}y^4 \right] \rho(r) d^3r \\
\Gamma_{xyyy} &= \int \left[\frac{5}{2}xy^3 - \frac{15}{8}(xyz^2 + x^3y) \right] \rho(r) d^3r \\
\Gamma_{xyyz} &= \int \left[\frac{15}{4}xy^2z - \frac{5}{8}(xz^3 + x^3z) \right] \rho(r) d^3r \\
\Gamma_{xyzx} &= \int \left[\frac{15}{4}xyz^2 - \frac{5}{8}(xy^3 + x^3y) \right] \rho(r) d^3r \\
\Gamma_{xzzx} &= \int \left[\frac{5}{2}xz^3 - \frac{15}{8}(xy^2z + x^3z) \right] \rho(r) d^3r \\
\Gamma_{yyyy} &= \int \left[y^4 + \frac{3}{8}(z^4 + x^4) - 3(y^2z^2 + x^2y^2) + \frac{3}{4}x^2z^2 \right] \rho(r) d^3r \\
\Gamma_{yyyz} &= \int \left[\frac{5}{2}y^3z - \frac{15}{8}(yz^3 + x^2yz) \right] \rho(r) d^3r \\
\Gamma_{yyzz} &= \int \left[\frac{3}{8}(9y^2z^2 - x^2z^2 - x^2y^2) - \frac{1}{2}(z^4 + y^4) + \frac{1}{8}x^4 \right] \rho(r) d^3r \\
\Gamma_{yzzz} &= \int \left[\frac{5}{2}yz^3 - \frac{15}{8}(y^3z + x^2yz) \right] \rho(r) d^3r \\
\Gamma_{zzzz} &= \int \left[z^4 + \frac{3}{4}x^2y^2 + \frac{3}{8}(y^4 + x^4) - 3(x^2z^2 + y^2z^2) \right] \rho(r) d^3r
\end{aligned} \tag{3.19}$$

so that the potential at any point P can now be rewritten as

$$\begin{aligned}
\Phi(P) = & \frac{q}{R} + \frac{X\mu_x + Y\mu_y + Z\mu_z}{R^3} + \\
& \frac{XXQ_{xx} + YYQ_{yy} + ZZQ_{zz} + 2(XYQ_{xy} + XZQ_{xz} + YZQ_{yz})}{R^5} + \\
& \frac{1}{R^7} [XXX\Omega_{xxx} + YYY\Omega_{yyy} + ZZZ\Omega_{zzz} + 3(XXYQ_{xxy} + \\
& XXZQ_{xxz} + XYYQ_{xyy} + XZZQ_{xzz} + YYZQ_{yyz} + YZZQ_{yzz}) + \\
& 6XYZQ_{xyz}] + \\
& \frac{1}{R^9} [XXXX\Gamma_{xxxx} + YYYY\Gamma_{yyyy} + ZZZZ\Gamma_{zzzz} + 4(XXXY\Gamma_{xxxy} + \\
& XXXZ\Gamma_{xxxz} + XYYY\Gamma_{xyyy} + XZZZ\Gamma_{xzzz} + YYYZ\Gamma_{yyyz} + \\
& YZZZ\Gamma_{yzzz}) + 6(XXYY\Gamma_{xxyy} + XXZZ\Gamma_{xxzz} + YYZZ\Gamma_{yyzz}) + \\
& 12(XXYZ\Gamma_{xxyz} + XYYZ\Gamma_{xyyz} + XYZZ\Gamma_{xyzz}) + \\
& \dots
\end{aligned} \tag{3.20}$$

We shall not dwell on the significance of equation (3.20) until Chapter 4, suffice it to say at this moment that it clearly reveals the electric multipole moments defined in equations (3.15, 3.16, 3.17, 3.18 and 3.19) to be the coefficients of a Taylor series

expansion. We will use this set of multipole moments throughout the remaining part of this thesis.

Before closing this section, we note another related definition of electric moment that surfaces in the literature from time to time, the “ordinal moments”, defined as

$$M_{i,j,k}(O) = \int x^i y^j z^k \rho(r) d^3r \quad (3.21)$$

commonly known as first moments when $i+j+k = 1$; second moments when $i+j+k = 2$, etc. The ordinal moments are the *de facto* primitive moments defined in Chapter 2. Although they can clearly be assembled into multipole moments, they are not multipole moments *per se*.

The Theory and Calculation of Molecular Orbitals

As a one-electron property, multipole moments are to be calculated for a given molecular electronic state. However, there is no exact solution of the Schrödinger equation for a many-electron molecule. In this section we outline the basic theory and technique that are used for calculating the electronic structure of a molecule. This begins with the calculation of the approximate molecular orbitals that will be used to calculate electronic properties like the molecular multipole moments under study.

1. The Hartree-Fock Theory

The electronic Hamiltonian of a molecule under Born-Oppenheimer approximation can be written in atomic units ($\hbar = m = e = 1$) as

$$\hat{H} = - \sum_i^n \frac{\nabla_i^2}{2} + \frac{1}{2} \sum_i^n \left(\sum_j^n \frac{1}{r_{i,j}} - \sum_\alpha^M \frac{Z_\alpha}{R_{i,\alpha}} \right) \quad (3.22)$$

where the first term is the electronic kinetic energy operator, and the following sum accounts for the Coulomb repulsion between pairs of electrons and the Coulomb attraction between the electrons and nuclei. The Schrödinger equation of the molecular electronic system is therefore

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad (3.23)$$

As mentioned, it is impossible to solve equation (3.23) for many-electron molecules exactly. Yet approximations can be made to attain an approximate solution from which a lot of the chemistry of a molecule can be uncovered. One such approximation is the Hartree-Fock approximation where a Slater determinant made of independent molecular spin orbitals $\{\phi_i(i), i = 1, n\}$ is used to approximate the molecular wavefunction

$$|\psi\rangle = |\phi_1(1)\phi_2(2) \cdots \phi_n(n)\rangle \quad (3.24)$$

For convenience, we restrict ourselves to a closed-shell formalism. There is no loss in generality, but only, for the moment, in complexity. The energy of the molecular system

from equation (3.23) is

$$\begin{aligned}
 E &= \sum_{i=1}^n \langle \phi_i(1) | -\frac{\nabla^2}{2} - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{R_{1,\alpha}} | \phi_i(1) \rangle + \\
 &\quad \frac{1}{2} \sum_{i,j=1}^n \langle \phi_i(1) \phi_j(2) | \frac{1}{r_{i,j}} | [\phi_i(1) \phi_j(2) - \phi_i(2) \phi_j(1)] \rangle \\
 &= \sum_{i=1}^n h_{ii} + \frac{1}{2} \sum_{i,j=1}^n (J_{ij} - K_{ij})
 \end{aligned} \tag{3.25}$$

where ϕ_i is a molecular orbital, h_{ii} is one-electron matrix element and J_{ij} and K_{ij} are two-electron Coulomb and exchange integrals, respectively.

The optimal energy E of equation (3.25) can be attained through the variation of the molecular orbitals while insuring their orthonormality. One minimizes the Lagrangian

$$L = E - \sum_{i,j} \epsilon_{ji} [\langle \phi_i | \phi_j \rangle - \delta_{ij}] \tag{3.26}$$

where ϵ_{ij} is a Lagrange multiplier,

$$\delta L = \delta \{ E - \sum_{i,j} \epsilon_{ji} [\langle \phi_i | \phi_j \rangle - \delta_{ij}] \} = 0 \tag{3.27}$$

to obtain the least $E = \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle \geq E_{exact}$ this leads to

$$\begin{aligned}
 &\sum_i^n \langle \delta \phi_i(1) | \{ h_{ii}(1) + \\
 &\quad \sum_j^n \langle \phi_j(2) | \frac{1}{r_{ij}} | (1 - P_{12}) \phi_j(2) \rangle \} | \phi_i(1) \rangle + \text{Complex Conjugate} \\
 &= \sum_i^n \langle \delta \phi_i(1) | \{ \sum_j^n \epsilon_{ji} \phi_j(1) \} + \text{Complex Conjugate}
 \end{aligned} \tag{3.28}$$

Since the variation is arbitrary, we must have

$$\{h_{ii}(1) + \sum_j^n [\hat{J}_j - \hat{K}_j]\} |\phi_i(1)\rangle = \sum_j^n \varepsilon_{ji} |\phi_j(1)\rangle \quad (3.29)$$

$$\hat{f}(1) |\phi_i(1)\rangle = \sum_j^n \varepsilon_{ji} |\phi_j(1)\rangle$$

where \hat{J}_j and \hat{K}_j are called Coulomb and exchange operators, and $\hat{f}(1)$ is the Fock operator. Since the Lagrange multiplier in this case is Hermitian, and the Fock operator is invariant under unitary transform, we can choose a set of spin orbitals that enable a diagonal form of Lagrangian multipliers, so that

$$\hat{f}(1) |\phi_i(1)\rangle = \varepsilon_i |\phi_i(1)\rangle \quad (3.30)$$

Equation (3.30) is called the Hartree-Fock equation, from which molecular orbitals of the given state $|\psi\rangle$ are obtained.

2. The LCAO-SCF Equations

For the Hartree-Fock equation (3.30) to have any practical use two problems remain to be solved: (1) what are the explicit forms of the molecular orbitals? and (2) how is the Fock operator constructed? The latter depends on the unknown molecular orbitals.

A successful solution to the first problem is the linear combination of atomic orbitals (LCAO) method established by Roothaan [73], which can be written as

$$|\phi_i\rangle = \sum_{\mu=1}^N C_{\mu i} |\chi_{\mu}\rangle \quad (3.31)$$

where $|\chi_\mu\rangle$'s are atomic orbitals usually centered at the constituent atoms of a molecular system, and the coefficients of the combination is to be determined from the formalism derived below.

The Hartree-Fock equation (3.30) in LCAO expansion takes the form

$$\hat{f} \sum_{v=1}^N C_{vi} |\chi_v\rangle = \varepsilon_i \sum_{v=1}^N C_{vi} |\chi_v\rangle \quad (3.32)$$

"bracketing" both sides of equation (3.32) by a bra $\langle\chi_\mu|$ (i.e. multiplying both sides by χ^* and integrating), we get

$$\sum_{v=1}^N F_{\mu v} C_{vi} = \varepsilon_i \sum_{v=1}^N S_{\mu v} C_{vi} \quad (3.33)$$

or in matrix form,

$$\mathbf{FC} = \mathbf{SC}\varepsilon \quad (3.34)$$

where \mathbf{F} is the Fock matrix, \mathbf{S} the overlap matrix, and \mathbf{C} the solution of molecular orbitals. Equation (3.34) is known as the Roothaan equation.

The overlap matrix \mathbf{S} is Hermitian, and in the absence of basis set dependence can be orthonormalized

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1} \quad (3.35)$$

through, for example, the Lowdin symmetric orthogonalization. Consider now a new coefficient matrix \mathbf{C}' related to the old one by

$$\mathbf{C}' = \mathbf{X}^{-1} \mathbf{C}, \quad \mathbf{C} = \mathbf{X} \mathbf{C}' \quad (3.36)$$

then Equation (3.34) can be written as

$$\mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{S}\mathbf{X}\mathbf{C}'\epsilon \quad (3.37)$$

and

$$\mathbf{X}^\dagger \mathbf{F}\mathbf{X}\mathbf{C}' = \mathbf{X}^\dagger \mathbf{S}\mathbf{X}\mathbf{C}'\epsilon \quad (3.38)$$

or simply,

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\epsilon \quad (3.39)$$

This procedure transforms the Roothaan equation into a standard matrix eigenvalue problem. Upon obtaining the solution of this matrix equation, electrons are assigned to basis MO's defined by the linear combination coefficient contained in a column of the \mathbf{C}' matrix. Such columns define occupied molecular orbitals. is said to be occupying that molecular orbital. In a calculation these occupations are of course assigned *a priori*. In the case discussed above every has an occupation of two or zero electrons. The formalism thus developed is called "restricted Hartree-Fock" (RHF) because every pair of α and β spin electrons are restricted to the same spatial molecular orbital.

The second problem posed in the beginning of this section leads to a strategy called Self-Consistent Field (SCF). In an SCF method, a starting guess of the molecular orbitals is given for computing the Fock matrix, then equation (3.39) is solved for a resulting set of molecular orbitals, which is then used to estimate a new set of orbitals that are then

used to compute the new Fock matrix to solve for a new set of molecular orbitals, and this iterative procedure continues cycle after cycle until self-consistency is achieved.

3. The INDO Technique

The Fock matrix elements of equation (3.39) for a restricted Hartree-Fock formalism can be expressed in the atomic basis as follows,

$$\begin{aligned}
 f_{\mu\nu} &= h_{\mu\nu} + \sum_a^{N/2} \sum_{\sigma\lambda} C_{\lambda a} C_{\sigma a}^* [2\langle\mu\sigma|\nu\lambda\rangle - \langle\mu\sigma|\lambda\nu\rangle] \\
 &= h_{\mu\nu} + 2 \sum_a^{N/2} \sum_{\sigma\lambda} C_{\lambda a} C_{\sigma a}^* [\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle] \\
 &= h_{\mu\nu} + \sum_{\sigma\lambda} P_{\lambda\sigma} [\langle\mu\sigma|\nu\lambda\rangle - \frac{1}{2}\langle\mu\sigma|\lambda\nu\rangle] \\
 &= h_{\mu\nu} + G_{\mu\nu}
 \end{aligned} \tag{3.40}$$

where the $P_{\lambda\sigma}$'s are the first order density matrix elements, defined by

$$P_{\lambda\sigma} = 2 \sum_a^{N/2} C_{\lambda a} C_{\sigma a}^* \tag{3.41}$$

and $h_{\mu\nu}$ is the one-electron Hamiltonian matrix element, and $G_{\mu\nu}$ is the two-electron matrix element composed of Coulomb and exchange integrals. The Fock matrix may be evaluated in several ways. Two major schools are: *ab initio*, in which all the integrals in equation (3.40) are evaluated; and semiempirical, in which some of the integrals are neglected and then the remaining ones are parametrized to reproduce experimental data. The work in this thesis falls into the second school.

In our calculation we invoke a basic approximation, known as the *Zero Differential Overlap* (ZDO) approximation, to neglect certain integrals,

$$\chi_\mu(1)\chi_\nu(1)d\tau(1) = 0, \quad \mu \neq \nu \quad (3.42)$$

whenever this differential is met in an integral over a symmetric operator. Thus the matrix of atomic overlap integrals becomes the unit matrix. The effect of this approximation on the one- and two-electron integrals, in terms of the number of such integrals and the physics they contribute to the theory, is pronounced. In particular, all three- and four-center Coulomb integrals are removed, and no exchange integrals remain, or

$$S_{\mu_A \nu_B} = \delta_{\mu\nu} \quad (3.43)$$

$$\langle \mu_A \lambda_C | \nu_B \sigma_D \rangle = \delta_{\mu\nu} \delta_{\lambda\sigma} \langle \mu \lambda | \mu \lambda \rangle \quad (3.44)$$

Throughout the development of quantum chemistry the ZDO approximation has been used to develop theory as well as to establish reliable models. Today there are numerous ZDO methods in use. They are all, in one way or another, based on the following approximations, the *Complete Neglect of Differential Overlap* (CNDO) approximation [74], the *Intermediate Neglect Differential Overlap* (INDO) approximation [75], and the *Neglect of Diatomic Differential Overlap* (NDDO) approximation [75]. The CNDO method utilizes the ZDO approximation for every integral evaluation encountered, while the INDO includes all one-center two-electron integrals and NDDO methods also include

all two-center hybrid integrals of the form $\langle \mu_A \nu_A | \sigma_B \lambda_B \rangle$ where the subscript refers to atomic center. All SCF calculations performed within this thesis were carried out at the INDO level of approximation and so it is the INDO method we will outline below.

Within the INDO approximation the Roothaan equation, relation (3.39), is constructed and iteratively solved as was previously discussed in the last section. The difference between INDO and *ab-initio* Hartree-Fock lies in the type of integral included, and their functional form, in the construction of the Fock matrix, with two caveats. The first being that the INDO method described here explicitly uses only the valence atomic orbitals, and the second being that in the LCAO–MO expansion only one basis function is used for each atomic orbital. Thus we will be describing, and working with, a *valence orbital minimum basis set* method. Below the INDO equations analogous to equation (3.40) are presented, μ, ν, σ and λ again label the atomic basis functions, $\{|\chi\rangle\}$, while A, B, C, \dots , label the atomic center the AO basis functions are associated with. The imposition of the INDO approximation on equation (3.40) leads to different forms for specific cases, and these are listed below.

1. Case $\mu = \nu; A = B$:

$$\begin{aligned}
 F_{\mu_A \mu_A} = & U_{\mu_A \mu_A} + \sum_{C \neq A} [P_{CC} \gamma_{AC} - V_{AC}] \\
 & + \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} [\langle \mu_A \lambda_A | \mu_A \sigma_A \rangle - \frac{1}{2} \langle \mu_A \lambda_A | \sigma_A \mu_A \rangle]
 \end{aligned}
 \tag{3.45}$$

2. Case $\mu \neq \nu$; $A = B$:

$$F_{\mu_A \mu_A} = \sum_{\lambda_A} \sum_{\sigma_A} P_{\sigma_A \lambda_A} [\langle \mu_A \lambda_A | \nu_A \sigma_A \rangle - \frac{1}{2} \langle \mu_A \lambda_A | \sigma_A \nu_A \rangle] \quad (3.46)$$

3. Case $\mu \neq \nu$; $A \neq B$:

$$F_{\mu_A \nu_B} = \beta_{\mu_A \nu_B} - \frac{1}{2} P_{\mu_A \nu_B} \gamma_{AB} \quad (3.47)$$

Several new terms were used in expressing equations (3.45) through (3.47), these are the terms used throughout the literature. We shall explain them below starting with the one-center core integral $U_{\mu_A \mu_A}$ of equation (3.45),

$$U_{\mu_A \mu_A} = \langle \mu_A | -\frac{1}{2} \nabla_i^2 + V_A | \mu_A \rangle \quad (3.48)$$

the one-center electron-nuclear attraction,

$$V_A = \frac{Z_A}{r_{iA}} \quad (3.49)$$

the first order atomic density P_{CC} is defined as,

$$P_{CC} = \sum_{\lambda_C} P_{\lambda_C \lambda_C} \quad (3.50)$$

the two-center two-electron γ_{AC} is defined as,

$$\gamma_{AC} = \langle \mu_A \lambda_C | \mu_A \lambda_C \rangle \quad (3.51)$$

and V_{AC} the two-center electron-nuclear attraction as

$$V_{AC} = \langle \mu_A | V_C | \mu_A \rangle \quad (3.52)$$

The $\beta_{\mu_A \nu_B}$ term is explained as replacing

$$\beta_{\mu_A \nu_B} = \langle \mu_A | -\frac{1}{2}\nabla^2 - V_A - V_B | \nu_B \rangle \quad (3.53)$$

There are many established methods to approximate the various terms above. The details of this subject can be found else where [76, 77]. It should be said the various integrals are replaced by functions of experimentally obtained parameters such as ionization potentials and electron affinities, with the exception of β in equation (3.53). The β term is, in many implementations, a totally empirical parameter and is usually obtained by varying it, while calculating a specific property or reproducing results of a higher level of theory, until acceptable results are obtained. Such is the case in this work. We shall obtain the SCF orbitals via two different INDO parametrization, one having been parameterized to reproduce molecular structures and the second to reproduce the low energy ultraviolet and visible absorption spectra of molecular systems.

Some Calculated Molecular Multipole Moments

As a one-electron property, a general multipole moment M can be calculated from

quantum mechanics as the expectation value for the state $|\psi\rangle$,

$$\begin{aligned}
 M &= \langle \psi | M | \psi \rangle \\
 &= \langle \phi_1(1)\phi_2(2) \cdots \phi_{2N}(2N) | M | \phi_1(1)\phi_2(2) \cdots \phi_{2N}(2N) \rangle \\
 &= \sum_{\mu, \nu}^N P_{\mu\nu} \langle \mu | M | \nu \rangle
 \end{aligned} \tag{3.54}$$

where the density matrix is obtained in this work from the SCF INDO calculation described in the preceding section, and the moment integrals over the atomic orbital basis are evaluated by using the method established in Chapter 2.

Multipole moments thus calculated are reported below for a variety of molecules. In general, the calculated value of a multipole moment tensor depends on which center is chosen to evaluate the moment integrals. To illustrate this, let us consider a system of many particles with the i -th particle having mass m_i and charge q_i located along the z -axis at a distance z_i from the origin O . The zeroth moments are $\sum_i m_i = M$ and $\sum_i e_i = q$, and are the total mass and total charge of the system. The first moments about the origin O are $\sum_i m_i z_i = C_z$ and $\sum_i e_i z_i = \mu_z$. If O is the center of gravity, C_z would vanish. To determine the effect on the moments of a change of origin, consider the dipole moment μ'_z relative to a new origin O' at the point $-Z$. Clearly

$$\mu'_z = \sum_i e_i (z_i + Z) = \mu_z + qZ \tag{3.55}$$

so that the dipole moment is independent of the origin only if q , the charge, is zero. The choice of origin is ideally the center of charge. However, it is usually chosen to be the

center of mass (COM) defined as $\frac{C_z}{M}$. The reason for this is that negative masses do not exist, so that no real system can have $M = 0$ and a COM can always be found, while the definition of center of charge varies. In molecular system, the center of mass is very close to the center of charge, as charge is generally proportional to the mass of an atom. The results reported below are all calculated from COM. Whenever possible, comparisons are made with either experimental or existing theoretical values, or both. For convenience, a conversion table is made as Table 3-2 for all the units involved in the following report.

H₂O

Water is fundamental in chemistry and biology, and it has always received a great deal of attention both theoretically and experimentally. Calculated electric multipole moments in this study are listed in Table 3-3. The calculation uses experimental geometry ($R_{O-H} = 0.958$ Å, $\angle HOH = 104.45^\circ$, and the oxygen is taken as the coordinate origin, and the two hydrogens are placed in the XY plane, pointing towards the negative X direction, where X is the C_2 axis (Figure 3 (A)). We have tested the performance of two sets of the two-electron integral INDO parametrization of γ , one which is fitted to produce good UV-Vis spectroscopy, and the other which is *ab initio* calculated γ used for obtaining geometry. Within each set of γ , we further tested the effect of neglecting two-center terms of the moment integrals. From this study we favor the inclusion of the two-center and the spectroscopic γ . Our results compare well with those reported in the existing

literature. The quadrupole calculation favors the experimental value from the reference c over that from the reference d. The lack of experimental higher moments makes other conclusions difficult.

Benzene

A favorite test to see if a theory can hold water (which our theory just did!) is to see if it holds benzene. Besides intriguing chemists for many years, it helped establishing many concepts and calculational models in molecular structure and spectra. Using HF-631G** optimized geometry with GAMESS, ($R_{C-C}=1.386$ Å, $R_{C-H}=1.076$ Å), the orientation of the input geometry is shown in Figure 3 (B). Benzene multipole moments are calculated and tabulated in Table 3-4. Notice that the dipole and octopole moments for benzene both vanish due to D_{6h} symmetry. We realized that the basis set of Zerner and Gouterman [78] used in ZINDO is not able to quantitatively reproduce the experimental moments. Zerner basis set is designed to reproduce geometries, and a better basis set for molecular moments is recommended by Rein, Nir and Swissler [79]. We use the Rein basis set for carbon, and the results compares very well with the experimental ones (Table 3-4). The most noticeable chemistry that can be explained from these results is the herring-shape structure of the benzene dimer in gas phase. The dimer would be a perfect perpendicular structure if only the quadrupoles are to be matched, but the hexadecapole interactions

exist as a perturbation to tilt the perpendicular dimer, giving the observed structure, as shown in Figure 4 (A).

Hexafluorobenzene

Calculated multipole moments of hexafluorobenzene, with its geometry optimized using the same procedure as that for benzene ($R_{C-C}=1.379$ A, $R_{C-F}=1.314$ A) are listed in Table 3-5. The input orientation is shown in Figure 3 (C). The most salient electronic feature of this molecule is the removal of electronic density along the ring. The calculated moments reflect this feature, reversing the sign of the moments from that observed for benzene. The Rein basis set does not have parameters for the fluorine atom. We therefore extrapolate the fluorine exponents from the existing C, O, and N exponents, and used $\zeta(2s)=2.7$ and $\zeta(2p)=2.9$, which, together with the Rein carbon exponents yields calculated moments again in very good agreement with experiments (Table 3-5). With the same argument for benzene dimers, we would predict the parallel docking structure for a Hexafluorobenzene-Benzene dimer (see Figure 4 (B)), as is observed in experiment.

Pyrazine

Table 3-6 gives calculated quadrupole and hexadecapole moments as calculated for pyrazine with the orientation shown in Figure 3 (D). The result is obtained for pyrazine imbedded in water solution, by using Self-consistent Reaction Field Model to be described in the next Chapter. The calculation uses the Zerner basis, default in ZINDO program.

It is marvelous that in solution the Zerner basis can adjust itself to give quadrupole moments comparable to those obtained from the very expensive calculation by Zeng, Woywod, Hush and Reimers [80]. This is very important because we will use default basis in solution calculations in the next chapter.

Table 3-2: The Conversion Factors for 1 a.u. Multipole Moments

Property	Conversion Factor
Electric Charge (Zeroth Moment)	$1.602189 \times 10^{-19} \text{ C (Coulomb)}$
	$4.803242 \times 10^{-10} \text{ esu}$
Dipole/First Moment	$8.478418 \times 10^{-30} \text{ m C}$
	$2.541765 \times 10^{-18} \text{ cm esu}$
	2.541765 D (Debyes)
Quadrupole/Second Moment	$4.486584 \times 10^{-40} \text{ m}^2 \text{ C}$
	$1.345044 \times 10^{-26} \text{ cm}^2 \text{ esu}$
	1.345044 B (Buckingham)
Octopole/Third Moment	$2.374197 \times 10^{-50} \text{ m}^3 \text{ C}$
	$7.117664 \times 10^{-35} \text{ cm}^3 \text{ esu}$
	7.117664 U (unnamed)
Hexadecapole/Fourth Moment	$1.256371 \times 10^{-60} \text{ m}^4 \text{ C}$
	$3.766505 \times 10^{-43} \text{ cm}^4 \text{ esu}$
	3.766505 N (noname)

Table 3-3: Calculated Multipole Moments of H₂O

Moments	This work				Rein <i>et al.</i>	exp	
	Spec. γ		Theor. γ				
	one-c	two-c	one-c	two-c			
μ (D)	2.306	2.235	2.239	1.903	2.52 ^a	1.85	
Q _{xx} Q _{yy} Q _{zz} (B)	-0.23 1.35 -1.12	-0.01 1.57 -1.56	-0.12 1.24 -1.12	0.03 1.43 -1.46	-0.32 ^b 1.00 -0.77	-0.13 ^c 2.63 -2.50	0.4 ^d 1.6 -2.0
Ω_{xxx} Ω_{xyy} Ω_{xzz} (U)	5.07 -8.46 3.34	8.72 -15.8 7.05	4.92 -7.95 3.02	7.93 -13.7 5.78	9.2 ^e -16.8 7.6		
Γ_{xxxx} Γ_{xxyy} Γ_{xxzz} Γ_{yyyy} Γ_{yyzz} Γ_{zzzz} (N)	-4.70 5.68 -0.98 -1.98 -3.70 4.68	-3.42 4.23 -0.81 -1.64 -2.59 3.41	-4.35 5.28 -0.93 -1.84 -3.44 4.37	-8.93 11.04 -2.11 -4.14 -6.91 9.02			

Table 3-3 Continued:

- a. Reference [79]
- b. Reference [32]
- c. From Magnetic Susceptibility, see reference [81]
- d. Reference [82]
- e. Reference [33]

Table 3-4: Calculated Multipole Moments of Benzene

Moments	This Work		Rabinowitz <i>et al.</i> ^c	Exp. ^d
	Zerner Basis ^a	Rein Basis ^b		
QXX	1.419	4.132	2.86	4.34
QYY	1.419	4.132	2.86	4.34
QZZ (B)	-2.838	-8.264	-8.69	-8.69
Γ XXXX	0.99	2.10		
Γ XXYY	0.33	0.70		
Γ XXZZ	-1.31	-2.80		
Γ YYYY	0.99	2.10		
Γ YYZZ	-1.31	-2.80		
Γ ZZZZ (NX100)	2.63	5.60		

a. Reference [78]

b. Reference [79]

c. Reference [32]

d. Reference [83]

Table 3-5: Calculated Multipole Moments of Hexafluorobenzene

Moments	This Work		Laidig ^c	Exp ^d
	Zerner Basis ^a	ERB ^b		
QXX	-8.766	-4.653	-4.718	-4.77
QYY	-8.766	-4.653	-4.718	-4.77
QZZ	17.532	9.306	9.434	9.54
(B)				
Γ XXXX	-5.56	-1.98		
Γ XXYY	-1.85	-0.66		
Γ XXZZ	-7.41	-2.64		
Γ YYYY	-5.56	-1.98		
Γ YYZZ	7.41	2.64		
Γ ZZZZ	-14.82	-5.27		
(NX100)				

a. Reference [78]

b. Expanded Rein Basis. See Reference [79] and text

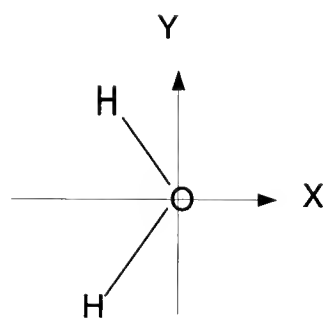
c. Reference [84]

d. Reference [85]

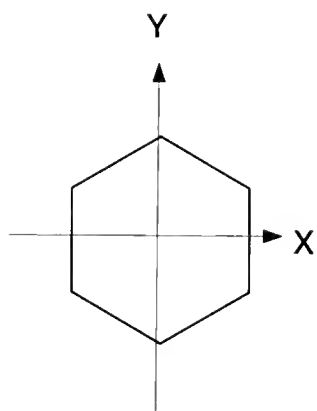
Table 3-6: Calculated Multipole Moments for Pyrazine in Water Solution

Moments	This Work	Hush ^a <i>et al.</i>
Q _{xx}	11.6	10.2
Q _{yy}	1.14	2.2
Q _{zz}	-12.8	-12.4
(B)		
Γ_{XXXX}	1.53	
Γ_{XXYY}	2.94	
Γ_{XXZZ}	4.47	
Γ_{YYYY}	1.04	
Γ_{YYZZ}	1.90	
Γ_{ZZZZ}	-6.37	
(NX100)		

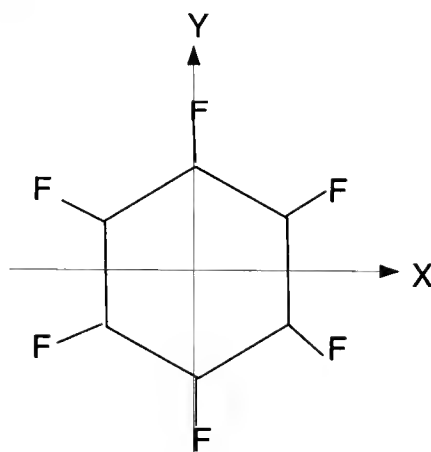
a. Reference [80]



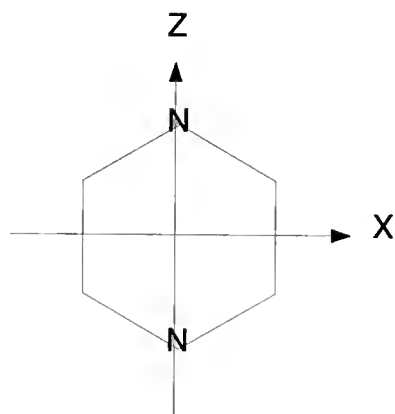
(A) Water



(B) Benzene



(C) Hexafluorobenzene



(D) Pyrazine

Figure 3: Input Molecular Orientations for Multipole Moment Calculations.

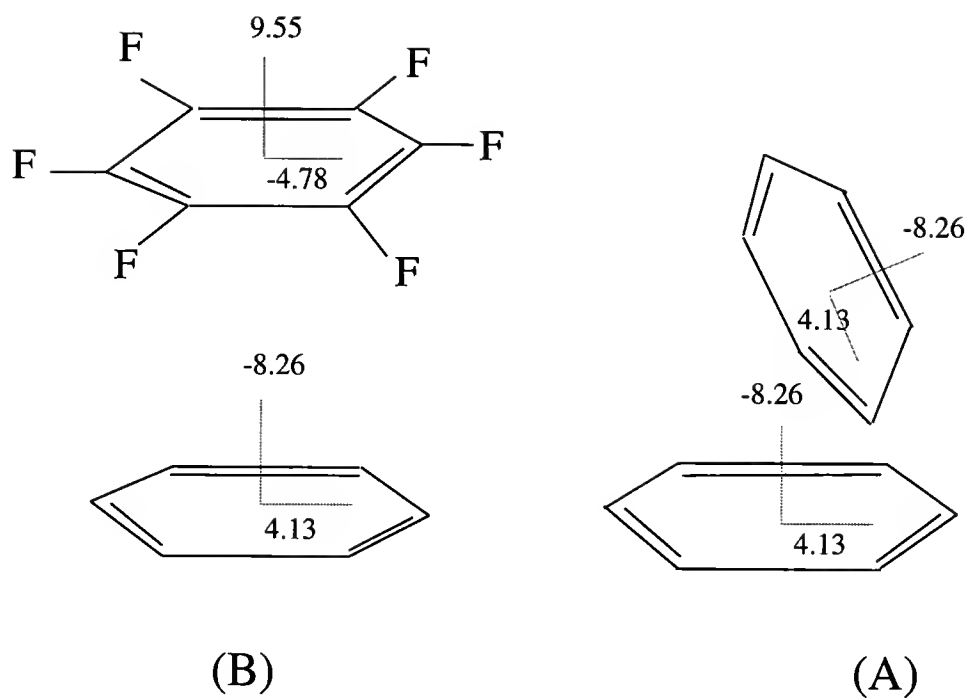


Figure 4: Dimer Structures of Hexafluorobenzene-Benzene and Benzene-Benzene Based on Multipole Moment Interpretations

CHAPTER 4

A SELF-CONSISTENT REACTION FIELD MODEL INCLUDING HIGH MOLECULAR ELECTRIC MULTIPOLE MOMENTS APPLIED TO THE CALCULATION OF MOLECULAR ELECTRONIC SPECTRA

As mentioned in Chapter 1, we are now going to examine the solvent effect on molecular electronic structure. As we know, most chemistry reactions take place in solution, and the solvation phenomenon is very challenging. A successful theoretical method should be able to calculate two basic experimental measurements: the solvation energy and the electronic spectroscopic shifts in solutions. We tackle the problem by approximating the solvent media as a dielectric continuum surrounding a quantum mechanical solute molecule, and by examining the electrostatic interactions between the molecular multipole moments and the solvent dielectric continuum.

The Reaction Field

We consider a solute molecule in a spherical cavity of radius a inside a solvent media with a uniform dielectric constant ϵ , as shown in Figure 5. The electrostatic potential of the solute molecule is expanded in multipole moments and allowed to interact with the dielectric continuum. For now, let us examine the potential at any point $P(r)$ outside the spheric cavity caused by a unit charge s distance away from the center of the sphere O .

The potential can then be expressed as

$$\begin{aligned}
 \phi_{out}(r) &= \frac{1}{r_e} = \frac{1}{\sqrt{s^2 - 2sr\cos\theta + r^2}} \\
 &= \frac{1}{r} \left(1 - 2\tau \frac{s}{r} + \frac{s^2}{r^2} \right)^{-\frac{1}{2}} \\
 &= \frac{1}{r} \left[1 + \frac{-\frac{1}{2}}{1} \left(-2\tau \frac{s}{r} + \frac{s^2}{r^2} \right) + \frac{-\frac{1}{2} \cdot \frac{3}{2}}{1 \cdot 2} \left(-2\tau \frac{s}{r} + \frac{s^2}{r^2} \right)^2 + \dots \right] \quad (4.1) \\
 &= \frac{1}{r} \left[1 + \tau \frac{s}{r} + \frac{3\tau^2 - 1}{r} \left(\frac{s}{r} \right)^2 + \frac{5\tau^3 - 3\tau}{2} \left(\frac{s}{r} \right)^3 + \dots \right] \\
 &= \frac{1}{r} \sum_{n=0}^{\infty} \left(\frac{s}{r} \right)^n P_n(\tau) = \sum_{n=0}^{\infty} \left(\frac{A_n}{r^{n+1}} \right) P_n(\tau)
 \end{aligned}$$

where we have used binomial expansion and Legendre polynomials, $P_n(\tau)$, and τ is the $\cos\theta$.

At a point inside the sphere equation (4.1) may not converge because s is not guaranteed to be larger than r . However, the potential must satisfy the Laplace equation, which, if the cavity is overall neutral, can be written as

$$\nabla^2 \phi_{in} = 0 \quad (4.2)$$

its general solution being

$$\phi_{in} = \sum_{n=0}^{\infty} \left(B_n r^n + \frac{D_n}{r^{n+1}} \right) P_n(\tau) \quad (4.3)$$

We then require that the potential on the sphere be single valued,

$$\phi_{in}(r) = \varepsilon \phi_{out}(r)|_{r=a} \quad (4.4)$$

and due to linear independence of Legendre polynomials, this gives, for a particular term $n = l$ in equations (4.1) and (4.3),

$$\frac{A_l}{a^{l+1}} = B_l a^l + \frac{D_l}{a^{l+1}} \quad (4.5)$$

and we further require continuity on the sphere,

$$\phi'_{in}(r) = \phi'_{out}(r)|_{r=a} \quad (4.6)$$

which gives, again for a particular term $n = l$,

$$-\varepsilon(l+1)A_l a^{-(l+2)} = lB_l a^{l-1} - (l+1)D_l a^{-(l+2)} \quad (4.7)$$

Equations (4.5) and (4.7) are standard boundary conditions for cavity models, and they give

$$B_l = \frac{(l+1)(1-\varepsilon)}{l+\varepsilon(l+1)} \cdot \frac{1}{a^{2l+1}} D_l = f_l(\varepsilon) D_l \quad (4.8)$$

With B_l determined by equation (4.8) we can write the potential inside the cavity as

$$\phi_{in}(r) = \sum_{n=0}^{\infty} \left(\frac{1}{r^{n+1}} + f_n(\varepsilon) r^n \right) D_n P_n(\tau) \quad (4.9)$$

where the second term is caused by the solvent dielectric interaction with the solute molecular multipole, and it is called the reaction field,

$$R = \sum_{n=0}^{\infty} f_n(\varepsilon) D_n r^n P_n(\tau) \quad (4.10)$$

the factor $f_l(\varepsilon)$ is called the reaction field factor, first derived by Kirkwood [86, 87].

The Interaction Energy in a Reaction Field

The interaction energy between the solute molecule with a quantum mechanically described charge distribution $\rho(r)$ and the dielectrically averaged solvent media is

$$\begin{aligned}
 E_{int} &= -\frac{1}{2} \int \rho(r) R d^3r \\
 &= -\frac{1}{2} \sum_{l=0}^{\infty} f_l D_l \int \rho(r) r^l P_l(r) d^3r \\
 &= -\frac{1}{2} \sum_{l=0}^{\infty} \sum_{m=-l}^l f_l M_l^m M_l^m
 \end{aligned} \tag{4.11}$$

where M_l^m 's are multipole moments of the solute molecule in a general form. In many applications the definition of the first moment differs from that of the second to gain considerable computational advantages, a point that we shall address more later.

The first term of equation (4.11) is the well-known Born term

$$E_{int}^{(1)} = -\frac{1}{2} \left(1 - \frac{1}{\varepsilon}\right) \left(\frac{1}{a}\right) q^2 \tag{4.12}$$

with q being the net charge of the solute molecule. The second term, first examined by Onsager [88], is known as the Onsager term,

$$E_{int}^{(2)} = -\frac{1}{2} \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)} \left(\frac{1}{a^3}\right) \mu^2 = -\frac{1}{2} g(\varepsilon) \mu^2 \tag{4.13}$$

with μ being the dipole moment of the solute molecule. The higher terms are all derived in this study, and they are

$$E_{int}^{(3)} = -\frac{3(\varepsilon - 1)}{2(3\varepsilon + 2)} \left(\frac{1}{a^5}\right) Q_{\alpha\beta}^2 = -h(\varepsilon) Q^2 \tag{4.14}$$

$$E_{int}^{(4)} = -\frac{4}{2} \frac{(\varepsilon - 1)}{(4\varepsilon + 3)} \left(\frac{1}{a^7} \right) \Omega_{\alpha\beta\gamma}^2 = -k(\varepsilon) \Omega^2 \quad (4.15)$$

$$E_{int}^{(5)} = -\frac{5}{2} \cdot \frac{(\varepsilon - 1)}{(5\varepsilon + 4)} \left(\frac{1}{a^9} \right) \Gamma_{\alpha\beta\gamma\sigma}^2 = -t(\varepsilon) \Gamma^2 \quad (4.16)$$

In the development of this work conceptual difficulty lies in the uncertainty on how to include higher terms into equation (4.11). Experience tells us these moments do not need to be in any particular definition as long as they are consistent throughout the same formulation, and we choose the form of equation (3.20) of Chapter 3 for two major reasons. The first reason is that the multipole moments as defined by Buckingham are already calculated and stored in our multipole moments analysis as described in Chapter 3. The second reason is that the coordinates appearing in equation (3.20) are primitive multipole moment operators, with their integrals in STO basis evaluated as described in Chapter 2 and stored as 'primitives'. It should also be added that equation (3.20) has aesthetic appeal with the numerical coefficients equal to the number of the possible permutations of the index, a feature we first mentioned in Chapter 3.

The Self-Consistent Reaction Model

When the solute molecule, the quantum mechanical motif that will be treated below, is placed in the reaction field, the energy of the system becomes

$$\begin{aligned} E_u &= E^0 - \frac{1}{2} \sum_{l,m} f_l M_l^m M_l^m \\ &= E^0 - \frac{1}{2} \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle \langle \psi | M_l^m | \psi \rangle \end{aligned} \quad (4.17)$$

where $|\psi\rangle$ is the state of the molecule, and E^0 the vacuum energy of the molecule. We form the functional

$$L = E^0 - \frac{1}{2} \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle \langle \psi | M_l^m | \psi \rangle - W(\langle \psi | \psi \rangle - 1) \quad (4.18)$$

where W is the Lagrangian multiplier. Variation of equation (4.18) proceeds as

$$\begin{aligned} \delta L &= \delta E^0 - W \delta \langle \psi | \psi \rangle - \frac{1}{2} \delta \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle \langle \psi | M_l^m | \psi \rangle \\ &= \langle \delta \psi | H_0 | \psi \rangle - \sum_{l,m} f_l \langle \delta | M_l^m | \psi \rangle \langle \psi | M_l^m | \psi \rangle - W \langle \delta \psi | \psi \rangle + c.c. \\ &= 0 \end{aligned} \quad (4.19)$$

which further lead to the Schrödinger equation of the molecular state

$$\left(H_0 - \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle M_l^m \right) |\psi\rangle = W |\psi\rangle \quad (4.20)$$

It is clear now W is the quantum mechanical energy of the solute molecule, given by

$$\begin{aligned} W &= \langle \psi | H_0 - \sum_{l,m} \langle \psi | M_l^m | \psi \rangle M_l^m | \psi \rangle \\ &= E_0 - \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle \langle \psi | M_l^m | \psi \rangle \end{aligned} \quad (4.21)$$

In a similar fashion as we did in Chapter 3, specifically, the equations (3.26) through (3.30), we approximate $|\psi\rangle$ by a Slater determinant composed of molecular orbitals $\{|\phi_i\rangle\}$ in the form of linear expansion of atomic basis functions. This procedure leads

to a Fock-like equation

$$\left(f^0 - \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle M_l^m \right) |\phi_i\rangle = \varepsilon_i |\phi_i\rangle \quad (4.22)$$

where ε_i is the solute molecular orbital energy, and f^0 is the vacuum Fock operator defined in equation (3.29) of Chapter 3. In the usually way, we can define the new Fock operator

$$f = f^0 - \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle M_l^m \quad (4.23)$$

to give

$$f |\phi_i\rangle = \varepsilon_i |\phi_i\rangle \quad (4.24)$$

Equation (4.24) is solved iteratively because the construction of the new Fock operator requires knowledge of the molecular orbitals both to form f_0 and to calculate $\langle \psi | M_l^m | \psi \rangle$. Upon an initial guess of the molecular orbitals, the iteration proceeds cycle after cycle until a self-consistency is achieved. This treatment of the molecule in solution is therefore known as the Self-Consistent Reaction Field (SCRF) model [40]. We have found later that faster convergence results when the moments are updated each cycle, as opposed to first converge the SCF and then the SCF and SCRF. Similarly we have found there is no advantage to perform the SCRF at the dipole level first, and gradually the quadrupole and higher moments after the initial calculation convergence.

Following the general approach of SCRF outlined above, there have been numerous theories developed recently. One of them, called “A theory”, views that the W from

equation (4.21) is the energy of the quantum motif, i.e. that of vacuum solute molecule and its interaction with the solvent. To counter the neglect of the solvent in the variation process, the system energy of equation (4.17) should add to W an extra term from the solvent,

$$\begin{aligned} E_u &= W + E_{c,c} \\ &= W + \frac{1}{2} \sum_{l,m} \langle \psi | M_l^m | \psi \rangle \langle \psi | M_l^m | \psi \rangle \end{aligned} \quad (4.25)$$

which yields again the energy of equation (4.17) and the $E_{c,c}$ herein is called the “solvent cost”, reflecting the fact that the solvent has lost energy to dissolve the solute. The second theory, called “B theory”, argues that the total energy of equation (4.17) is should be given by the energy functional [89], and therefore the Fock operator equation (4.23) becomes,

$$f = f^0 - \frac{1}{2} \sum_{l,m} f_l \langle \psi | M_l^m | \psi \rangle M_l^m \quad (4.26)$$

In B theory the solvent cost is included in equation (4.26) in the SCF energy variations.

The Configuration Interaction Calculation for Electronic Spectra

Solvents affect molecular electronic structure, causing sometimes sizable energy shifts. The excited states of molecules are often calculated using the configuration interaction (CI) method. Conceptually, CI is a straightforward method of linear variation over the determinants of many-electron wave functions. Again we desire to solve the Schrödinger equation by assuming an approximate solution. In the CI approach the

approximate wave function $|\Psi\rangle$ is expanded as a linear combination of Slater determinants

$|\psi\rangle$

$$\Psi = \sum_s^N C_s \psi_s \quad (4.27)$$

Where the C_s 's, are the parameters which are varied to make $E[\Psi]$ stationary. N is the number of expansion functions. We examine,

$$E[\Psi] = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (4.28)$$

in which H in equation (4.28) above is the electronic Hamiltonian. This leads to the general matrix eigenvalue equation

$$\mathbf{HC} = \mathbf{SC}\epsilon \quad (4.29)$$

where

$$H_{st} = \langle \psi_s | H | \psi_t \rangle \quad (4.30)$$

and

$$S_{st} = \langle \psi_s | \psi_t \rangle \quad (4.31)$$

The N linearly independent eigenvectors \mathbf{c}_p , the columns of \mathbf{C} , can be chosen to be orthonormal with respect to \mathbf{S} ,

$$\mathbf{c}_p^\dagger \mathbf{S} \mathbf{c}_q = \sum_{s,t}^N c_{sp}^* S_{st} c_{tq} = \delta_{pq} \quad (4.32)$$

leading to the simple eigenvalue equation

$$\mathbf{H}\mathbf{c}_p = \mathbf{c}_p E_p \quad (4.33)$$

We now need to find the basis over which CI is to be performed. A very natural and intuitive choice of the determinantal wave functions $\{|\psi\rangle\}$ is constructed in the following fashion,

$$|\Psi\rangle = C_0|\psi_0\rangle + \sum_i^{occ} \sum_a^{vir} C_i^a |\psi_i^a\rangle + \sum_{i<j}^{occ} \sum_{a<b}^{vir} C_{ij}^{ab} |\psi_{ij}^{ab}\rangle + \sum_{i<j<k}^{occ} \sum_{a<b<c}^{vir} C_{ijk}^{abc} |\psi_{ijk}^{abc}\rangle + \dots \quad (4.34)$$

where $|\psi_0\rangle$, in the first term of equation (4.34), is the Hartree-Fock reference function obtained in the SCF procedure previously described. The set of functions $\{|\psi_{i,j,\dots}^{a,b,\dots}\rangle\}$ are spin-adapted configurations generated by removing electrons from the occupied spin molecular orbital $\{|\phi_i\rangle, |\phi_j\rangle, \dots\}$ and placing them in the virtual, or unoccupied, spin orbital $\{|\phi_a\rangle, |\phi_b\rangle, \dots\}$. These are known collectively as the electronic excitations from the molecular ground state described by the Hartree-Fock theory. If the summation in equation (4.34) is carried to its limit, the calculation so performed is said to be a full CI calculation. Computational resources usually limit the summation of equation (4.34) to low “order”, resulting in the CI Singles (CIS) procedure, CI Singles and Doubles (CISD), and so on. Even with CI truncated in this fashion it is not unusual to reduce it even further by limiting the size of the active space. That is, to limit the number of

active orbitals from which electrons are removed or into which they are placed, usually centered around the highest energy occupied molecular orbital (HOMO) and the lowest energy unoccupied molecular orbital (LUMO), or the “HOMO–LUMO gap”. For the work in this thesis the CI expansion, equation (4.34), is truncated at the second term, and thus belongs to CIS model. The popular ZINDO code has been parametrized for spectroscopy at this level of theory [90].

In these calculations the CI eigenvalues of equation (4.33)

$$E_1 \leq E_2 \leq E_3 \cdots \leq E_N \quad (4.35)$$

can be shown to be upper bounds to the corresponding true eigenvalues of the CI Hamiltonian, and they approximate the energy of excited molecular states. Furthermore, if additional configuration functions are added to the expansion, equation (4.27), each eigenvalue E_p^{N+1} of the $(N + 1)$ term expansion satisfies the bracketing theorem

$$E_{p-1}^{(N)} \leq E_p^{(N+1)} \leq E_p^{(N)} \quad (4.36)$$

and as $\{|\psi_N\rangle\}_{E_p^N}$ approaches completeness the $\{E_p^N\}$ must approach the exact eigenvalues of the CI Hamiltonian from above. It should be noted, however, that there is no variational theorem for the transition energies *between* states.

We consider $|\psi_0\rangle$, and one singly excited configuration function, $|\psi_i^a\rangle$, or

$$|\Psi_{CIS}\rangle = (C_0|\psi_0\rangle + C_i^a|\psi_i^a\rangle) \quad (4.37)$$

and proceed to evaluate $\langle \Psi_{CIS} | H | \Psi_{CIS} \rangle$ for its lowest eigenvalue and associated eigenvector we obtain the matrix eigenvalue problem

$$\begin{pmatrix} \langle \psi_0 | H | \psi_0 \rangle & \langle \psi_0 | H | \psi_i^a \rangle \\ \langle \psi_i^a | H | \psi_0 \rangle & \langle \psi_i^a | H | \psi_i^a \rangle \end{pmatrix} \begin{pmatrix} C_0 \\ C_i^a \end{pmatrix} = E_0 \begin{pmatrix} C_0 \\ C_i^a \end{pmatrix} \quad (4.38)$$

It is obvious that any mixing of the diagonal elements is through the off-diagonal element

$$\langle \psi_0 | \hat{H}_{el} | \psi_i^a \rangle = \langle i | \hat{h} | a \rangle + \sum_r [\langle ir | ar \rangle - \langle ir | ra \rangle] \quad (4.39)$$

or its adjoint. The ia -th element of the Fock operator, again in the basis of spin molecular orbitals, is given by

$$\langle \phi_i | \hat{f} | \phi_a \rangle = \langle i | \hat{h} | a \rangle + \sum_r [\langle ir | ar \rangle - \langle ir | ra \rangle] \quad (4.40)$$

Notice that the right-hand-side of both equation (4.39) and equation (4.40) are identical and thus

$$\langle \psi_0 | H | \psi_i^a \rangle = \langle \phi_i | \hat{f} | \phi_a \rangle \quad (4.41)$$

Now by definition solving the Hartree-Fock eigenvalue problem requires the off-diagonal elements of the Fock matrix to vanish, or upon solution

$$\langle \phi_i | \hat{f} | \phi_a \rangle = 0 \quad (4.42)$$

and then so must equation (4.39). The above exercise is an example of *Brillouin's Theorem* [91]. Stated in words as, singly excited Slater determinates $|\psi_i^a\rangle$ will not

directly interact with a closed-shell Hartree-Fock reference determinant $|\psi_0\rangle$ through the electronic Hamiltonian, or

$$\langle\psi_0|H|\psi_i^a\rangle = 0 \quad (4.43)$$

$\{|\psi_i^a\rangle\}$ leaves the closed-shell Hartree-Fock reference unchanged. This is a desirable feature for the INDO technique that has already included the experimental data in its parametrization. This approach to the CI method has proven quite successful for the calculation of the low energy ultraviolet, and visible, absorption spectra of molecular systems.

Up to this stage the discussion of CI has been completely general in the sense that it has not dealt with the specific forms of the Hamiltonian. When a molecule is placed in the reaction field, the CI Hamiltonian matrix elements are

$$\begin{aligned} H_{IJ} &= \langle\psi_I|H_0 - \sum_{l,m} f_l \langle\psi_0|M_l^m|\psi_0\rangle M_l^m|\psi_J\rangle \\ &= \langle\psi_I|H_0|\psi_J\rangle - \sum_{l,m} f_l \langle\psi_0|M_l^m|\psi_0\rangle \langle\psi_I|M_l^m|\psi_J\rangle \end{aligned} \quad (4.44)$$

where H_0 is the vacuum Hamiltonian, and in the formalism we follow the A theory without losing generality. The rest of the CI implementation follows the discussion in a straightforward fashion. There are, however, two important modifications to the CI energy after the diagonalization.

The first deals with the absorption process in a dielectric media. According to Classius-Mosotti, the bulk solvent dielectric constant ϵ has the following relation

$$\frac{\epsilon - 1}{(l + 1)\epsilon + l} = \frac{D' - 1}{(l + 1)D' + l} + \frac{n^2 - 1}{(l + 1)n^2 + l} \quad (4.45)$$

with D' being the contribution due to the slow motion of solvent reorientation, and n , the solvent index of reflection, reflecting the electron polarization. In this spirit, we factor equation (4.10) into two parts

$$f_l(\epsilon) = f_l(D') + f_l(n^2) \quad (4.46)$$

We further assume that in an absorption process, generally of the order of 10^{-18} seconds, there is no motion of the solvent molecules, but that the electronic polarization is instantaneous. The energy transition is then modified and it becomes

$$\Delta E_I = \frac{1}{2} \sum_{l,m} f_l(n) (\langle \psi_0 | M_l^m | \psi_0 \rangle \langle \psi_I | M_l^m | \psi_I \rangle - |\langle \psi_I | M_l^m | \psi_I \rangle|^2) \quad (4.47)$$

where the first term removes the incorrect term included in using the SCRF orbitals in forming the CI matrix, and the second adds the response of the electron polarization $-\frac{1}{2}f_l(n)\langle \psi_I | M_l^m | \psi_I \rangle$ to the excited state multipoles $\langle \psi_I | M_l^m | \psi_I \rangle$. Note that this term does not allow for complete relaxation which would otherwise be described by $-\frac{1}{2}f_l(\epsilon)\langle \psi_I | M_l^m | \psi_I \rangle$.

The second modification has to do with the solvent cost. Similar to equation (4.25), we must add to the quantum mechanical result an extra term, that is,

$$W_I^A = \langle \psi_I | H | \psi_I \rangle + \frac{1}{2} \sum_{l,m} f_l(\epsilon) \langle \psi_0 | M_l^m | \psi_0 \rangle \langle \psi_I | M_l^m | \psi_I \rangle \quad (4.48)$$

to count for the solvent cost in the excited state.

With the above discussion, we are able to calculate the spectroscopic absorption $|\psi_0\rangle \rightarrow |\psi_I\rangle$,

$$\begin{aligned} W_I^A - W_0^A &= [\langle \psi_I | H | \psi_I \rangle - \langle \psi_0 | H | \psi_0 \rangle] + \\ &\quad \frac{1}{2} \sum_{l,m} f_l(\epsilon) \langle \psi_0 | M_l^m | \psi_0 \rangle [\langle \psi_I | M_l^m | \psi_I \rangle - \langle \psi_0 | M_l^m | \psi_0 \rangle] + \\ &\quad \frac{1}{2} \sum_{l,m} f_l(n) \langle \psi_I | M_l^m | \psi_I \rangle [\langle \psi_0 | M_l^m | \psi_0 \rangle - \langle \psi_I | M_l^m | \psi_I \rangle] \end{aligned} \quad (4.49)$$

where the first term is a direct result of the CI, the second term is due to the solvent cost, and the third term is due to instantaneous electronic relaxation. And similarly, discounting the solvent cost term, we can write for B theory

$$\begin{aligned} W_I^B - W_0^B &= [\langle \psi_I | H | \psi_I \rangle - \langle \psi_0 | H | \psi_0 \rangle] + \\ &\quad \frac{1}{2} \sum_{l,m} f_l(n^2) \langle \psi_I | M_l^m | \psi_I \rangle [\langle \psi_0 | M_l^m | \psi_0 \rangle - \langle \psi_I | M_l^m | \psi_I \rangle] \end{aligned} \quad (4.50)$$

A second way to view the absorption process is to assume that the ground state and excited states are intimately coupled to form a mean field, and the states feel the molecular charge distribution through the instantaneous electron polarization of the solvent. In such

a case, the energy of a state $|\psi_k\rangle$ is shifted by

$$\frac{1}{2}f_l(n^2)[|\langle\psi_0|M_l^m|\psi_0\rangle|^2 - \langle\psi_k|M_l^m|\psi_k\rangle(\langle\psi_0|M_l^m|\psi_0\rangle + \langle\psi_I|M_l^m|\psi_I\rangle)]/2 \quad (4.51)$$

and this leads to “A1 theory”,

$$\begin{aligned} W_I^{A1} - W_0^{A1} &= [\langle\psi_I|H|\psi_I\rangle - \langle\psi_0|H|\psi_0\rangle] + \\ &\frac{1}{2} \sum_{l,m} f_l(\varepsilon) \langle\psi_0|M_l^m|\psi_0\rangle [\langle\psi_I|M_l^m|\psi_I\rangle - \langle\psi_0|M_l^m|\psi_0\rangle] - \\ &\frac{1}{4} \sum_{l,m} f_l(n^2) [\langle\psi_0|M_l^m|\psi_0\rangle - \langle\psi_I|M_l^m|\psi_I\rangle]^2 \end{aligned} \quad (4.52)$$

and to B1 theory

$$\begin{aligned} W_I^{B1} - W_0^{B1} &= [\langle\psi_I|H|\psi_I\rangle - \langle\psi_0|H|\psi_0\rangle] - \\ &\frac{1}{4} \sum_{l,m} f_l(n^2) [\langle\psi_0|M_l^m|\psi_0\rangle - \langle\psi_I|M_l^m|\psi_I\rangle]^2 \end{aligned} \quad (4.53)$$

Recently a new theory, called “C theory”, is developed and tested in this study. This theory, based on A theory, calculate the energy for the final state $|\psi_f\rangle$ as

$$\begin{aligned} E_f &= W_f + \sum_{l,m} f_l(n^2) \langle\psi_f|M_l^m|\psi_f\rangle [\langle\psi_0|M_l^m|\psi_0\rangle - \langle\psi_f|M_l^m|\psi_f\rangle] \\ &+ f_l(n^2) \langle\psi_f|M_l^m|\psi_f\rangle^2/2 + f_l(D') \langle\psi_0|M_l^m|\psi_0\rangle^2/2 \end{aligned} \quad (4.54)$$

where the difference from A theory is that the final state assumes the ground state geometrical contribution in the solvent cost energy. Its absorption is expressed as

$$E_f^C - E_0^C = W_f - W_0 - \frac{1}{2} \sum_{l,m} f_l(n^2) (\langle\psi_f|M_l^m|\psi_f\rangle - \langle\psi_0|M_l^m|\psi_0\rangle)^2 \quad (4.55)$$

and in the mean field we have for “CI theory”,

$$E_f^{C1} - E_0^{C1} = W_f - W_0 + \frac{1}{4} \sum_{l,m} f_l(n^2) (\langle \psi_f | M_l^m | \psi_f \rangle - \langle \psi_0 | M_l^m | \psi_0 \rangle) \\ (3 \langle \psi_0 | M_l^m | \psi_0 \rangle - \langle \psi_f | M_l^m | \psi_f \rangle) \quad (4.56)$$

Results

In this section results of the performance of high moments in the SCRF-CI model are reported. Our Hartree-Fock reference function is obtained by using the semiempirical INDO/S technique. In the SCRF model, the convenient reference for multipole expansion is at the center of mass (as discussed in the last chapter). The cavity radius is obtained from the mass density, for which we have molecular cavity volume

$$V = \frac{4}{3} \pi a^3 = \frac{M}{d N_A} \quad (4.57)$$

$$a = 0.7346 (M/d)^{\frac{1}{3}} \quad \text{\AA}$$

where M is the molecular weight in amu, d is the mass density of the solute (g/cm³) and a, of course, the cavity radius. Unless specified, we assume the reference standard in our calculations below.

H₂O

Although H₂O does not have interesting UV-Vis spectroscopic feature, it is a favorite molecule to test the convergence of the SCRF model. Our result for H₂O solvent cost energy in H₂O solution is shown in Table 4-7. The convergence this work achieved is

satisfactory from dipole to hexadecapole expansion, and it compares well with the results from Multiconfigurational SCRF calculation by Mikkelsen, Argen, Jensen and Helgaker [15].

We do not hesitate to point out here that there is clearly an error in reference [15], where Table II and Table IV do not agree. And Judging from our values, their dipole level calculation may be reported incorrectly.

Acetone

The $n - \pi^*$ UV-Vis spectroscopic solvent shifts of acetone is calculated with all theories A, A1, B, B1, C, C1, at different cavity radii. Our starting point for the cavity radii is the mass density radius, 2.84 Å. The calculation is done first at the dipole level, and then include higher moments up to hexadecapole. The results are listed in Tables 4-8 to 4-13 and the cavity radius dependence of calculated solvent shifts with C1 theory is shown in Figure 6.

It is a general feature that solvent shift decreases as the cavity radius increases, as shown in Figure 6 for the case of C1 theory. At the radius region examined, all previous theories A, A1, B, and B1 underestimate the solvatochromore shift significantly for acetone. Only theories C and C1 give results that compare well with experiment. Within the same theory, dipole moment expansion usually underestimates the experimental shift,

and the inclusion of higher moments brings additional blue shift to yield better agreement with experiment.

Pyrazine

Solvent shifts of pyrazine are calculated at quadrupole and hexadecapole levels of multipole expansion with all theories at cavity radius 3.61 Å, a radius that is found in our experience appropriate for diazene series of molecules. The results are reported in Table 4-14.

Pyrazine is an interesting molecule, because it has not been able to be studied by the SCRF methods that include only dipole moment expansions. Our conclusions made earlier regarding the performance of multipole moments with difference theories for acetone molecule is once again confirmed here by the results in Table 4-14.

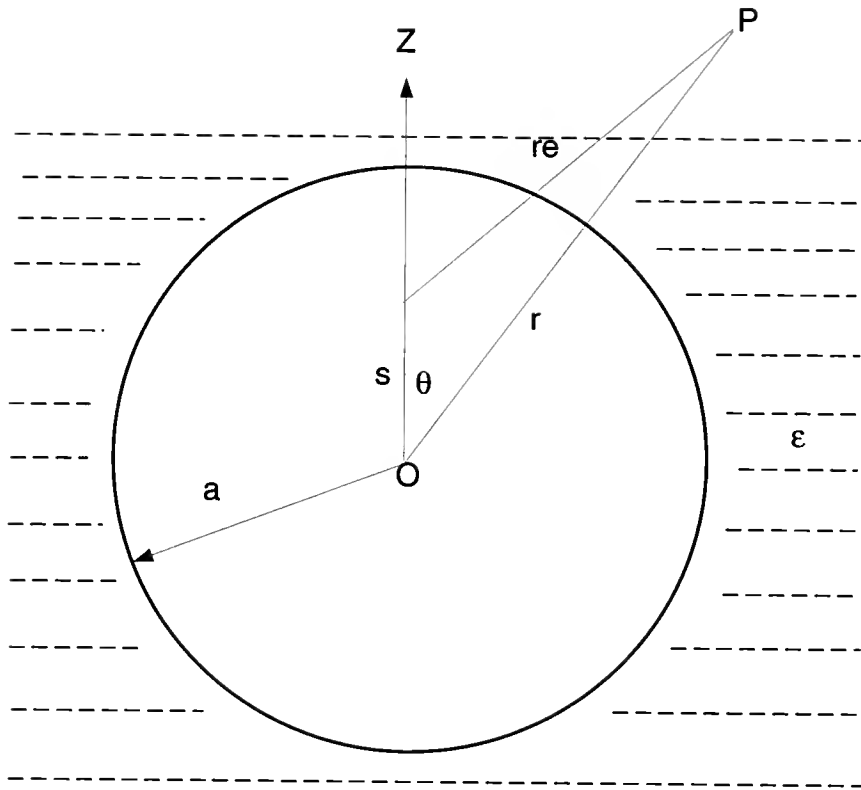


Figure 5: Spherical Cavity Model

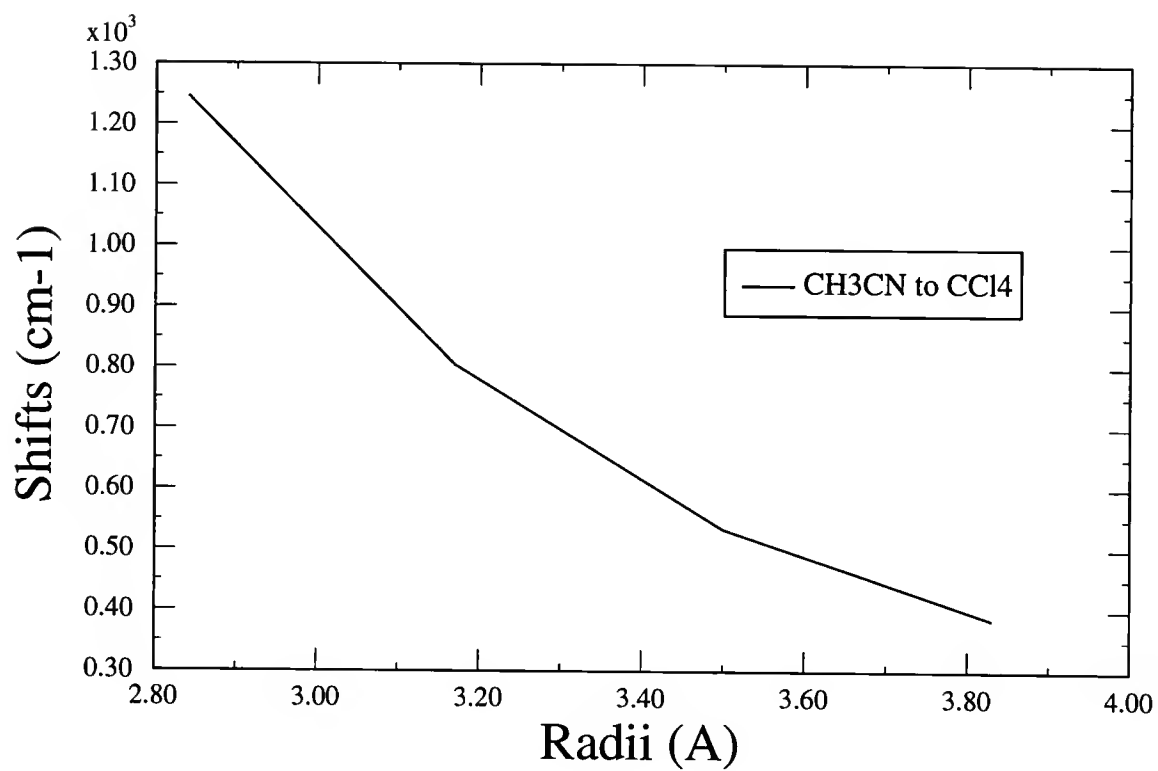


Figure 6: Solvent Shift Dependence on Cavity Radii: C1 theory for acetone.

Table 4-7: H₂O solvent cost energy convergence in H₂O solution

Multipole Expansion	This Work	Mikkelsen ^a
r = 3.5 a.u.		
Monopole	0	0
Dipole	0.01079	0.01239
Quadrupole	0.00238	0.00466
Octopole	0.00104	0.00138
Hexadecapole	0.00029	0.00037
Total	0.01450	0.01880
r = 4.0 a.u.		
Total	0.00828	0.00864
r = 4.5 a.u.		
Total	0.00552	0.00542

a. Reference [15]

Table 4-8: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory A.

Radii (A)		2.84	3.17	3.50	3.83
CCL4	Dip	29583	29487	29428	29390
	Hex	29721	29562	29470	29416
	Exp				
CHCL3	Dip	29699(116)	29558(71)	29476(48)	29424(34)
	Hex	29914(193)	29668(106)	29537(67)	29462(46)
	Exp	(540) ^a			
CH3CN	Dip	29789(206)	29610(123)	29509(81)	29447(57)
	Hex	30071(350)	29753(191)	29581(117)	29494(78)
	Exp	(940 - 1140) ^a			

a. Reference [92].

Table 4-9: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory A1.

Radii (A)		2.84	3.17	3.50	3.83
CCL4	Dip	29281	29277	29276	29276
	Hex	29331	29291	29287	29281
	Exp				
CHCL3	Dip	29377(96)	29340(63)	29320(44)	29309(33)
	Hex	29504(173)	29390(99)	29345(58)	29325(44)
	Exp	(540) ^a			
CH3CN	Dip	29499(218)	29418(141)	29374(98)	29348(72)
	Hex	29699(368)	29515(224)	29424(137)	29378(97)
	Exp	(940 - 1140) ^a			

a. Reference [92].

Table 4-10: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory B.

Radii (Å)		2.84	3.17	3.50	3.83
CCL4	Dip	29710	29583	29502	29448
	Hex	29863	29672	29556	29481
	Exp				
CHCL3	Dip	29895(185)	29709(126)	29592(90)	29515(67)
	Hex	30137(274)	29843(171)	29672(116)	29565(84)
	Exp	(540) ^a			
CH3CN	Dip	30048(338)	29813(230)	29666(164)	29569(121)
	Hex	30364(501)	29987(315)	29769(213)	29634(153)
	Exp	(940 - 1140) ^a			

a. Reference [92].

Table 4-11: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory B1.

Radii (Å)		2.84	3.17	3.50	3.83
CCL4	Dip	29428	29384	29356	29337
	Hex	29489	29417	29374	29349
	Exp				
CHCL3	Dip	29607(179)	29508(124)	29446(90)	29405(68)
	Hex	29748(259)	29587(170)	29492(118)	29434(85)
	Exp	(540) ^a			
CH3CN	Dip	29799(371)	29641(257)	29542(186)	29476(139)
	Hex	30033(285)	29769(352)	29616(242)	29523(174)
	Exp	(940 - 1140) ^a			

a. Reference [92].

Table 4-12: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory C.

Radii (Å)		2.84	3.17	3.50	3.83
CCL ₄	Dip	29606	20502	29439	29399
	Hex	29731	29563	29480	29423
	Exp				
CHCL ₃	Dip	30015(409)	29776(274)	29633(194)	29542(143)
	Hex	30309(578)	29929(366)	29723(243)	29599(176)
	Exp	(540) ^a			
CH ₃ CN	Dip	30475(869)	30076(574)	29842(403)	29694(295)
	Hex	30954(1223)	30334(771)	29992(512)	29788(365)
	Exp	(940 - 1140) ^a			

a. Reference [92].

Table 4-13: Calculated acetone $n - \pi^*$ solvent shifts (cm-1): Theory C1.

Radii (Å)		2.84	3.17	3.50	3.83
CCL4	Dip	29301	29293	29287	29285
	Hex	29331	29291	29294	29287
	Exp				
CHCL3	Dip	29693(392)	29558(265)	29478(191)	29426(141)
	Hex	29889(558)	29651(360)	29532(238)	29462(175)
	Exp	(540) ^a			
CH3CN	Dip	30186(885)	29884(591)	29707(420)	29596(311)
	Hex	30577(1246)	30095(804)	29828(534)	29672(385)
	Exp	(940 - 1140) ^a			

a. Reference [92].

Table 4-14: Pyrazine $n-\pi^*$ Solvent Shift (cm-1): From Acetonitrile to Diethyl Ether.

Theory ($r = 3.61 \text{ \AA}$)	Diethyl Ether		Acetonitrile	
	Quad.	Hex.	Quad.	Hex.
C	31092	31105	31202(110)	31227(122)
C1	31037	31054	31148(111)	31175(121)
B	31047	31054	31093(52)	31066(12)
B1	30987	30994	31040(53)	31046(52)
A	31019	31025	31063(44)	31074(49)
A1	30964	30957	31009(45)	31015(58)
Exp ^a	31610		31740	(130)

a. Reference [93]

CHAPTER 5

CONCLUSIONS

In this thesis we have examined molecular multipole moments and their applications in the Self-Consistent Reaction Field (SCRF) model. In the course of this study we have established and tested both the reliability and the speed of the method and computational programs used for the calculation of molecular multipole moments and the SCRF model that includes high orders of electrostatic interactions.

Although the computation of the STO integrals we established is quite general, we have calculated molecular electric multipole moments using the semiempirical Intermediate Differential Overlap (INDO) wavefunction at both the Hartree-Fock and correlated levels of theory. A general approach on multipole moment integrals arising in the computation is developed over Slater-type orbitals (STO) and presented with explicit formulas in this thesis. A computational package implementing this approach is produced in this study and in our experience it is fast and reliable. Molecular multipole moments calculated with the existing INDO minimum basis set agree well even into the high orders with results in the available literature (Tables 3-3 to 3-6), although these results are rare. Quantitative agreement with experiment is excellent if the basis set proposed by Rein, Adams, Nir, and Swisler [79] is used for the heavy atoms (Tables 3-4 and 3-5). For atoms for which the Rein basis are not available an estimate based on the Rein exponents

may be made and this proves to be quite satisfactory (Table 3-5). While most *ab initio* and numerical calculations of high moments [94, 95, 20] require very sophisticated basis sets and high levels of theory, we have achieved the same quality results with inexpensive INDO wave function at the Hartree-Fock level of theory and simple basis set that only requires different exponents for the s and p orbitals. Higher moments from both theory and experiment are rare in the literature, and we can not comment on moments higher than the octopole that we obtained. We might expect some extended basis set to be necessary for these high moments. On the other hand we might expect the high moments to be sensitive to the basis set long range behavior. This behavior is correct for the STOs we use, but the Gaussian orbitals used in most *ab initio* works decay too rapidly.

Calculated molecular multipole moments are then included in the SCRF model through the first order multipole expansion of electrostatic potentials between the solute molecule and solvent dielectric continuum media. Computations are implemented in the Zerner's INDO (ZINDO) package to calculate solvent shift of electronic spectra by using the spectroscopically parametrized Configuration Interaction Singles (CIS) method. Spectroscopic shifts unaccountable previously by the Onsager terms are now produced to accord well with experiment. We found that in the Pyrazine case higher moments up to hexadecapole is necessary to better uncover the experimental solvent shift (Table 4-14).

Most spectroscopic shifts in chemistry are blue-shift, the results of this study uni-

formly confirms this trend with the inclusion of higher moments (Tables 4-8 to 4-13). Many SCRF calculations that are based only on the dipolar Onsager term, and, indeed, the SCRF at the dipole moment level has proved to be the most important in solvation chemistry. But it should be realized that the Onsager term is inadequate in cases in which (1) the molecule possesses no dipole moment and (2) the contribution of higher moments are significant, as this study finds. The contribution from the higher moments is, of course, a matter of the multipole moment expansion convergence. We found the quadrupole contribution is often significant and its inclusion is often necessary to get good agreement with experiment, as for example, in the case of pyrazine.

We found the previously proposed theories A, A1, B, and B1 to be inferior to our new C and C1 theories as outlined in the text. The C and C1 theories, combined with necessary high order multipole moment expansion promises to be the best approach to solvation chemistry that we can have at hand.

It should be pointed out that the development in this study concerns only the solute molecule constrained to a spherical cavity. We realize that spherical cavity may not be the most accurate shape to describe a molecular cavity imbedded in solution, and therefore a multicavity model has been examined earlier [49]. We believe a comparison of the results of multicavity model and the elliptical cavity model [96] with high multipole moments included would be interesting. And further, a new basis set that produces more accurate

high moments might be test for use in predicting electronic spectra at the CIS level used most often in ZINDO. Previous studies shown that the accuracy of spectral transitions is not sensitive to the basis change, but the solvent shift is.

Little needs to be said about the myriad usefulness of molecular multipole moments that can now be reliably calculated with the INDO wavefunctions, or in fact, any wavefunction that employs STOs. Only a few developments concerns us immediately. First we can expand the basis set of Rein to the atoms not yet studied by Rein to make accurate multipole moments available to a greater variety of molecules; In a separate development, basis functions can established to preverve the singularities and proper long range behavior of the total wavefunction by using asymptotic exponents proposed by Monkhorst [97]. With attractive features at long range asymptotic exponential basis functions can offer a viable alterntive to the Rein basis set if their severe limitation for molecular system can be overcome [98]. Secondly, we will be able to calculate the electrostatic potentials of a molecule in an STO basis along the lines of Culberson and Zerner [99], but now, supposedly with higher accuracy. And thirdly, we are now able to study molecular interactions quantitatively (even for very large molecules [11]) with the formalism established by Isnard, Robert and Galatry [90], and Glendening [100]. It has come to our attention that this third development, particularly that implemented by Glendening, has already been used for computing potential energies to complement

the empirical Leonard-Jones formula used in molecular dynamics simulations of large molecules [100], and it should be valuable for the combined quantum mechanics and classical molecular mechanics approach to molecular solvent effect already in progress in this research group [101].

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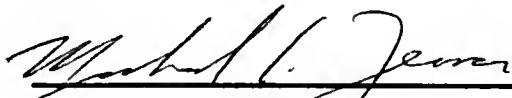
BIOGRAPHICAL SKETCH

Xuehe Zheng was born an ox in the First People's Hospital of Nanchang City. He was born into an intellectual's family under labor reform, yet, as his mother told him, into a magnificent sunset. The night before he was born, his grandmother dreamed that her husband led home an ox; she was worried, and asked: "Why do you bring home an ox? We have nothing to feed him!"


The hardy life of an ox feeds on grass, yet it contributes things more valuable. Perhaps such has been the philosophy of this ox. Xuehe Zheng proceeded through high school, under a virtual segregation from any privileges, but remained the top student. He was fortunate enough to be allowed to take the college entrance examination and attend Jiujiang Teachers College and Jilin University, when the new regulation of admission was first established after ten years of cultural revolution.

He joined the faculty of the Chemistry Department at the Jiujiang Teachers College in 1984. The following year he won a fellowship from the Higher Education Commission and joined the Quantum Theory Project at the University of Florida. He later applied and was admitted to graduate study there, and he has become a very stubborn Gator.

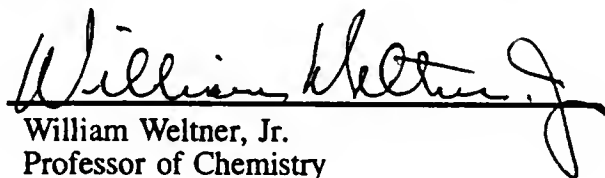
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Professor of Chemistry and Physics

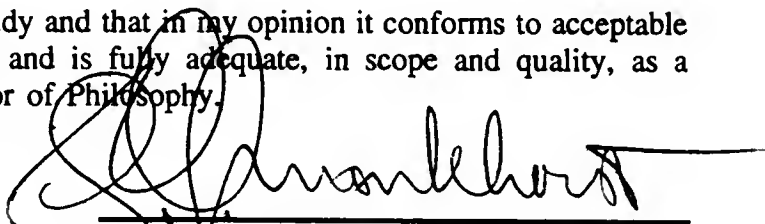
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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